

To the best of our knowledge, this is the first example of the use of neutron diffraction to establish the absolute configuration of a molecule made asymmetric by isotopic substitution.

*Acknowledgment.* We are very much indebted to Dr. A. L. Patterson of the Institute for Cancer Research who coordinated the project, and Drs. H. A. Levy and H. G. Smith of the Oak Ridge National Laboratory for their continued interest in and discussion of this work.

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## The Parahydrogen Conversion over Synthetic Ruby

Sir:

The purpose of this communication is to report some new information on the chromia and chromia-alumina catalyst systems.

Palladium-diffused hydrogen, equilibrated at  $-196^\circ$ , was passed over powdered synthetic ruby containing 1.1 atom % chromium and having a specific surface of about 2 m.<sup>2</sup>, with negligible porosity. Space velocity was 240 (STP)/min., at 1 atm. The temperature was changed at  $1^\circ/\text{min.}$  Reactor inlet and outlet were protected by liquid nitrogen traps.

Cooling the ruby from  $529^\circ$  gave the parahydrogen conversion pattern labeled "ruby-cooling" in Figure 1.

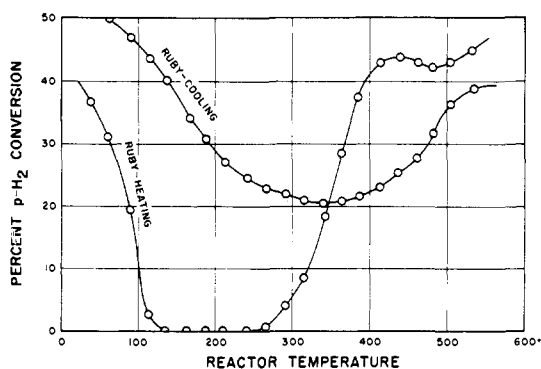


Figure 1. Parahydrogen conversion over powdered synthetic ruby. The cooling curve is reversible, but only if contamination is rigidly prevented.

Prompt subsequent heating showed the "ruby-cooling" curve to be reversible. Hydrogen-deuterium exchange under the same experimental conditions was, as expected, slight at  $25^\circ$ , moderate at  $500^\circ$ .

Impregnated chromia-alumina dehydrogenation catalyst containing 5 atom % chromium was now substituted for the ruby. It was assumed that, in this system, and at the concentration given, about one in twenty of the chromium ions present was on the surface.<sup>1</sup> The space velocity was therefore increased

(1) R. P. Eischens and P. W. Selwood, *J. Am. Chem. Soc.*, **69**, 1590 (1947).

(by decrease of catalyst mass) 1000-fold, so that the number of chromium ions accessible to molecular hydrogen was roughly equal to that in the ruby. The activity of the chromia-alumina catalyst below  $200^\circ$  was about 10-fold less than that of the ruby but, starting near  $300^\circ$ , the activity quickly rose to at least 1000-fold greater than the ruby.

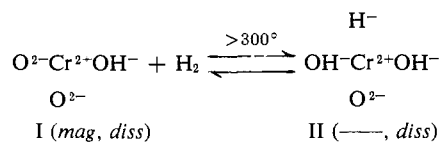
After the ruby stood at  $25^\circ$  overnight in hydrogen, but not protected by cold traps, the activity pattern was that labeled "ruby heating" in Figure 1. Cooling from  $500^\circ$  produced the "ruby-cooling" pattern, but interruption of heating in the 120 to  $280^\circ$  region produced a system inert at  $25^\circ$  and down to  $-196^\circ$ . Chromia-alumina also showed this poisoning effect, but in modified form.

Exposure of an active sample to laboratory air caused complete loss of activity, which was slowly recovered in hydrogen at  $500^\circ$ .

Powdered (chromia-free) synthetic sapphire gave no activity at  $25^\circ$ , and a small, slowly increasing activity above  $450^\circ$ .

In ruby the concentration of chromium ion pairs is almost certainly negligible.<sup>2</sup> In supported chromia-alumina catalysts the situation is quite different, most of the chromia being present in small, widely separated aggregates.<sup>1,3</sup> The results given show that dissociative activity in chromia-alumina occurs with Cr-Cr adjacency, and that chromium ions far from other chromiums are, even though accessible to the reactant, relatively inactive. The small low-temperature magnetic conversion over the supported chromia is possibly related to Cr-Cr exchange (or superexchange) interaction, which is diminished, but still measurable,<sup>1</sup> in these systems.

It is premature to consider in detail the mechanisms for activation, poisoning, and recovery of ruby activity, but the following suggestions may be useful. The high magnetic activity shown at  $25^\circ$  suggests excellent accessibility of molecular hydrogen to the chromium ions. Following current views,<sup>4,5</sup> it is assumed that activated ruby contains surface  $\text{Cr}^{2+}$  ions, but that these have only three adjacent neighbors (two  $\text{O}^{2-}$  and one  $\text{OH}^-$ ). Such dissociative activity as exists over ruby is then representable as a reversible, heterolytic chemisorption



The notations (*mag, diss*) mean the kind of catalytic activity, magnetic or dissociative or both, expected from the several kinds of sites shown. The mechanism is analogous to a view concerning alkane dehydrogenation over chromia.<sup>6</sup>

If the ruby is exposed to a trace of water vapor (or perhaps merely stands at room temperature) the

(2) Private communication from Professor Arthur L. Schawlow.

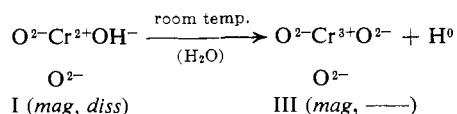
(3) D. E. O'Reilly, *Advan. Catalysis*, **12**, 31 (1960).

(4) J. Givaudon, E. Nagelstein, and R. Leygonie, *J. chim. phys.*, **47**, 304 (1950).

(5) S. W. Weller and S. E. Voltz, *J. Am. Chem. Soc.*, **76**, 4695, 4701 (1954).

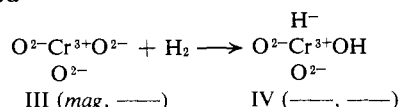
(6) R. L. Burwell, A. B. Littlewood, M. Cardew, G. Pass, and C. T. H. Stoddart, *ibid.*, **82**, 6272 (1960).

chromium undergoes oxidation,<sup>7</sup> but apparently without blocking the chromium ion. The product III



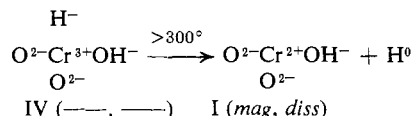
has only slightly less magnetic activity than I, but it has little dissociative activity. The reaction shown is possibly catalyzed by water through the sequence of adsorption, conversion to 2OH<sup>-</sup>, and desorption. The atom of hydrogen may be expected to dimerize quickly, and especially so if, as proposed, active species migrate over alumina surface.<sup>8</sup>

Heating species III in hydrogen causes a complete loss of activity at 120° (or somewhat higher). This is represented



This, rather than depletive reduction,<sup>7</sup> seems probable as the source of hydrogen chemisorption which occurs on chromia gel<sup>9</sup> in the 200° region.

Finally, above 300°, the chromium is reduced, with catalytic reactivation



The rapid recovery of activity above 300° is associated with renewed access of molecular hydrogen to the chromium.

The poisoning action of laboratory air on species I is probably due to a combination of oxidation of the chromium to Cr<sup>3+</sup>, plus adsorption and conversion to OH<sup>-</sup>, thus effectively blocking all access to the paramagnetic ion.<sup>7</sup> Oxidation to the diamagnetic hexavalent chromium seems less probable in the ruby surface.

Use of a dilute solid solution of reasonably well-characterized structure, and relative freedom from surface contamination, appears to bridge, in part, the gap between those studies made under conditions of exceptional surface cleanliness, and those on practical catalysts. The method is applicable to systems other than ruby.

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(7) L. L. Van Reijen, W. M. H. Sachtler, P. Cossee, and D. M. Brouwer, Third International Congress of Catalysis, Amsterdam, 1964, preprint I 52.

(8) J. L. Carter, P. J. Lucchesi, J. H. Sinfelt, and D. J. C. Yates, ref. 7, preprint I 37.

(9) R. L. Burwell, Jr., and H. S. Taylor, *J. Am. Chem. Soc.*, **58**, 697 (1936).

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## Infrared Spectra of Adenosine Triphosphate Complexes in Aqueous Solution

Sir:

From a recent paper,<sup>1</sup> the impression could arise that coordination of metal ions to adenosine triphosphate (ATP) in aqueous solution would not produce any significant shifts in the infrared absorptions of the triphosphate group other than those which accompany loss of a proton, so that no information regarding the mode of binding in ATP complexes could be derived from their infrared spectra. In order to clarify that significant and structurally interpretable shifts indeed occur upon complex formation of ATP<sup>4-</sup>,<sup>2</sup> infrared absorption curves of ATP<sup>4-</sup> and, as an example, of its zinc complex, measured in D<sub>2</sub>O and H<sub>2</sub>O solutions, are presented in Figure 1.

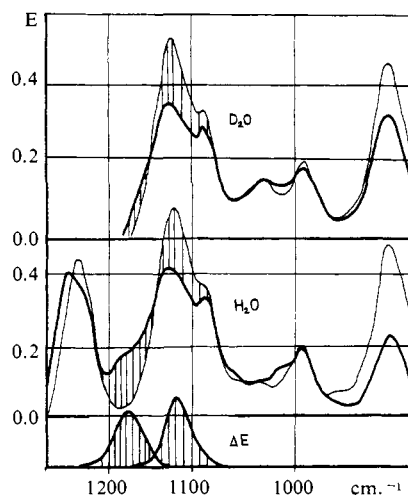


Figure 1. Effect of complex formation with Zn<sup>2+</sup> on infrared absorption spectrum of ATP<sup>4-</sup> in D<sub>2</sub>O and H<sub>2</sub>O solutions: thin lines, absorption of 0.2 M Na<sub>4</sub>ATP at pH 8.8 and pD 8.8; heavy lines, absorption of 0.2 M Na<sub>4</sub>ATP + 0.2 M ZnCl<sub>2</sub> at pH 7.7 and pD 7.9 (27 μ IRTRAN cells, Beckman IR 8).

All the triphosphate absorption bands of ATP<sup>4-</sup> observable in the 900–1300-cm.<sup>-1</sup> region in D<sub>2</sub>O and H<sub>2</sub>O solution show, on complex formation with Zn<sup>2+</sup>, characteristic changes. At the pH and pD given, no species other than ATP<sup>4-</sup> and ZnATP<sup>2-</sup> (*i.e.*, no ATP protonated species) are present to measurable extents. Coordination of Zn<sup>2+</sup> produces a pronounced change of the absorption band at 1120 cm.<sup>-1</sup>. From the spectra in H<sub>2</sub>O solution it is evident that the decrease of the main peak at 1120 cm.<sup>-1</sup> is accompanied by an equivalent increase of absorption at 1175 cm.<sup>-1</sup>; complex formation with Zn<sup>2+</sup> obviously shifts one of the components of the 1120-cm.<sup>-1</sup> ATP absorption to higher wave numbers by 55 cm.<sup>-1</sup>. In D<sub>2</sub>O very much the same features are observed as in H<sub>2</sub>O except that the increase of absorption at 1175 cm.<sup>-1</sup> is indeed scarcely observable in D<sub>2</sub>O. This is most likely due to the fact that the steep rise of D<sub>2</sub>O absorption at 1150–1200 cm.<sup>-1</sup> obscures this spectral region.

The symmetric >PO<sub>2</sub><sup>-</sup> and asymmetric -PO<sub>3</sub><sup>2-</sup> stretching vibrations contribute to the triphosphate ab-

(1) F. L. Khalil and T. L. Brown, *J. Am. Chem. Soc.*, **86**, 5113 (1964).

(2) H. Brintzinger, *Biochim. Biophys. Acta*, **77**, 343 (1963).