

of this reaction is 11,000 cal./mole of active centers of the enzyme and is independent of the pH. This value differs considerably from that estimated by Kistiakowsky and Lumry, and is more accurate because of a more direct method of determination and a greatly improved reproducibility of measurements. The inhibition by sulfite, similarly to the inhibition by phosphate ions described by Niemann and Harmon, has been found to be competitive with urea.

We also find that certain organic sulfur compounds, such as sodium benzene sulfinate, inhibit the enzyme in the same manner as sulfite ions, and our experiments in this direction are continuing.

HARVARD CHEMICAL LABORATORY  
12 OXFORD STREET  
CAMBRIDGE 38, MASS.

J. F. AMBROSE  
G. B. KISTIAKOWSKY  
A. G. KRIDL

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#### MANGANESE CARBONYL

Sir:

The synthesis of volatile manganese compounds, believed to be carbonyls of manganese, has been accomplished by reducing manganese iodide with Grignard reagent under pressure of carbon monoxide. The general reaction technique has been that described for the preparation of chromium carbonyl by Owen, English, Cassidy and Dundon.<sup>1</sup>

Identification of the volatile manganese compounds as carbonyls has been made by the observation that they behave chemically as would be predicted from a consideration of their relation to the carbonyls of iron and cobalt, and by mass spectrometric analyses which show characteristic peaks predicted for manganese carbonyl.

Qualitative tests for manganese in distillation fractions, etc., have been made by decomposing the samples with nitric acid and developing the permanganate color with the highly specific persulfate test.

The ethereal solutions from the synthesis reactions have been subjected to repeated washings with dilute hydrochloric acid and distilled water to remove manganese halide, and unreacted manganese iodide, and to destroy any organomanganese compounds possibly formed in the reaction.

(1) B. B. Owen, *et al.*, *THIS JOURNAL*, **69**, 1723 (1947).

Tests for halogen in these washed solutions have been negative. The solutions then have been dried, and the solvent ether removed by evaporation at low temperatures on a vacuum line. Some volatile manganese generally distills with the ether and may be collected in a trap at  $-80^{\circ}$ . Less volatile ether-soluble manganese compounds remain in the residue. The compounds also are soluble in *n*-pentane.

Manganese is extracted from an ether solution of manganese carbonyl by aqueous alkali. Acidification of the resulting solution in a stream of carbon monoxide releases a volatile manganese compound which can be collected in a subsequent trap at  $-80^{\circ}$ . This may be the  $\text{Mn}(\text{CO})_4\text{H}_2$  which has been predicted.<sup>2</sup>

The addition of mercuric chloride to an ethereal solution of manganese carbonyl results in a slow evolution of gas and a precipitate containing manganese and mercury. Heating the dried precipitate liberates free mercury, leaving a residue containing manganese. This behavior is consistent for a mercuric salt of manganese carbonyl hydride.

The peaks observed for manganese carbonyl in the mass spectrometer are strong, occur at regular intervals following a pattern similar to that of other metal carbonyls, and do not correspond to any of the predictable impurities. The observation of the fragments  $\text{Mn}_2(\text{CO})_5^+$ ,  $\text{Mn}_2(\text{CO})_6^+$  and  $\text{Mn}_2(\text{CO})_7^+$ , formed in the spectrometer by electron bombardment, indicates the existence of a dimeric manganese carbonyl but does not define the formula since it is not uncommon for the parent peak to be absent in a mass spectrometric analysis. Peaks corresponding to  $\text{Mn}^+$ ,  $\text{MnC}^+$ ,  $\text{MnCO}^+$ ,  $\text{MnC}(\text{CO})^+$ ,  $\text{Mn}(\text{CO})_2^+$ ,  $\text{MnC}(\text{CO})_2^+$ ,  $\text{Mn}(\text{CO})_3^+$ , and  $\text{MnC}(\text{CO})_3^+$  also have been observed. The appearance of the intermediate fragments containing C atoms is typical of the mass spectra of all metal carbonyls investigated so far and will be reported later.

Transparent crystals (containing manganese) have been isolated by subliming solvent-free material in a stream of carbon monoxide. The quantity of material has been small and no pure compounds have been identified as yet.

GENERAL ELECTRIC  
RESEARCH LAB.  
SCHENECTADY, N. Y.

DALLAS T. HURD  
GEORGE W. SENTELL, JR.  
FRANCIS J. NORTON

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(2) Blanchard, *Chem. Rev.*, **21**, 35 (1937).