

is suggested by our findings that one supplier's methanol (Fisher, Certified Reagent) contains spectroscopically detectable benzene which is removable with low efficiency by rectification and that 0.2 wt. per cent. of benzene added to purified Eastman "Spectro Grade" methanol reduced $G(\text{CH}_2\text{O})$ to 5.5. No benzene was detectable in the latter before or after purification but it is possible that the relatively poor precision of our $G(\text{CH}_2\text{O})$ values may reflect variable trace amounts of benzene. The present high value of $G(\text{CH}_2\text{O})$ suggests that CH_2O may be formed in a short chain reaction.

A detailed study of oxygenated methanolic solutions is now in progress. A survey of the effect of water on peroxide production from other substrates has been initiated.

CHEMISTRY DEPARTMENT
BOSTON UNIVERSITY
BOSTON 15, MASS.

NORMAN N. LICHTIN
LYNN A. ROSENBERG
MASASHI IMMAMURA

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THE INFRARED SPECTRUM AND EVIDENCE FOR THE STRUCTURE OF A NEW METAL CARBONYL¹

Sir:

The infrared spectra, structures, and hybridizations of metal pentacarbonyls derived from the hexacarbonyls of Cr, Mo, and W are of considerable interest. Several workers^{2,3,4} have postulated their existence as intermediates in the production of hexacarbonyl derivatives of the type $\text{M}(\text{CO})_5(\text{L})_n$ by ultraviolet irradiation (L = ether, nitrile, amine, etc.). Such reactions are thought to be initiated by the mechanism



We have obtained evidence to support this view.

0.02 mmole of $\text{W}(\text{CO})_6$ was dissolved in 2 ml. of a specially purified 1:4 methylcyclohexane-isopentane mixture, and the resulting solution was placed under nitrogen in a thin quartz tube and cooled to 77° K. The resulting glass was irradiated until a yellow color appeared. At the instant the glass was melted the solution was withdrawn from the tube, and the infrared spectrum was taken immediately. The spectrum showed peaks at 2075 (w), 1936 (s), and 1912 (ms) cm^{-1} in the carbonyl stretching region; such a spectrum is characteristic of a square pyramid of five carbonyl groups about the metal atom.⁵ The species was found to have a half-life of about two minutes at room temperature. The experiment was repeated using *n*-hexane as the solvent, and bands were found at 1935 and 1911 cm^{-1} .

Of the four species which one might reasonably expect to be the product of the photolysis, one, $\text{W}_2(\text{CO})_{10}^-$, may be rejected immediately because its spectrum shows carbonyl stretching bands⁶ at 1944, 1906, and 1882 cm^{-1} . The monomer $\text{W}(\text{CO})_5^-$ may also be discounted because extensive electron spin resonance studies show no evidence

(1) Supported by A.E.C. contract AT-(40-1)-2434.

(2) L. E. Orgel, *Nature*, **191**, 1387 (1961).

(3) G. R. Dohson, M. A. El Sayed, I. W. Stolz and R. K. Sheline, *Inorg. Chem.*, **1**, 526 (1962).

(4) W. Strohmeier, *Chem. Ber.*, **94**, 3337 (1961).

(5) L. E. Orgel, *Inorg. Chem.*, **1**, 25 (1962).

(6) W. Hieber, W. Beck and G. Braun, *Angew. Chem.*, **72**, 795 (1960).

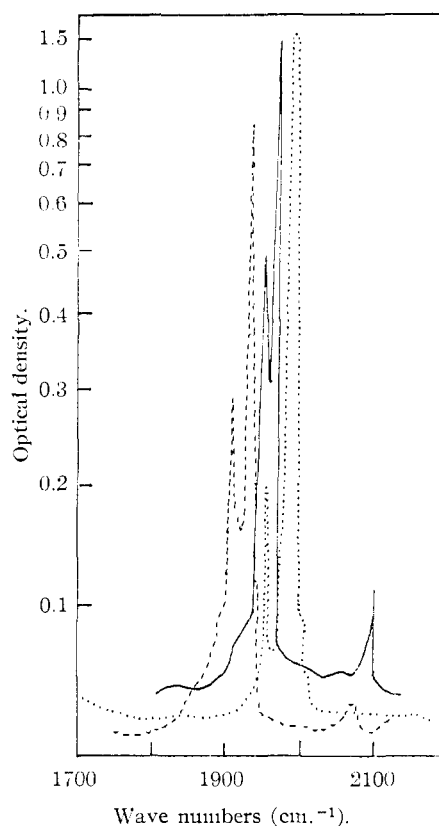


Fig. 1.—Carbonyl stretching region of infrared for $\text{W}(\text{CO})_6$, $\text{W}(\text{CO})_5$ and $\text{W}(\text{CO})_5(\text{CHCH})$: $\text{W}(\text{CO})_6$; —, $\text{W}(\text{CO})_5(\text{CHCH})$; ----, $\text{W}(\text{CO})_5$.

for the existence of unpaired electrons in our species. The structure $\text{W}(\text{CO})_5^-$ is also open to serious question because it is highly unlikely that the other product of such a photodissociation, CO^{++} , could exist long enough to permit the observed reversibility³ of the reaction and because one would expect the carbonyl stretching bands for such a complex to be at much lower frequencies than those observed. The carbonyl stretching frequencies for $\text{Fe}(\text{CO})_5$ are at 2034 and 2014 cm^{-1} and for $\text{Mn}(\text{CO})_5^-$ are at 1898 and 1863⁷ cm^{-1} , illustrating the pronounced lowering of frequency when even one electron is introduced into a five-coordinated structure. Finally, the solubility of the complex in non-polar solvents is a strong argument against any of the three charged structures discussed.

In support of the proposed structure we have analytically and spectrophotometrically proven that $\text{W}(\text{CO})_5(\text{CH}_3\text{CN})$ is immediately formed when acetonitrile is introduced into a solution containing the species. Furthermore, the spectrum of $\text{W}(\text{CO})_5(\text{CHCH})$ shows carbonyl stretching bands at 2097, 1967, and 1954 cm^{-1} , in line with the expectation that the poor charge donating ability of acetylene coupled with its outstanding ability to accept any excess charge accumulated on the metal atom should slightly increase the CO bond order from that found in the postulated species. We believe that $\text{W}(\text{CO})_5$ is a d^2sp^3 hybrid and that the vacant p orbital is responsible for its extreme reactivity.

(7) W. F. Edgell, *J. Am. Chem. Soc.*, **82**, 1254 (1960).

Similar experiments with $\text{Fe}(\text{CO})_5$ have yielded a band at 1834 cm.^{-1} which we believe to be due to the formation of a tetracoordinated iron carbonyl. Work on this complex and the lower complexes of Cr and Mo is continuing.

DEPARTMENT OF CHEMISTRY
FLORIDA STATE UNIVERSITY
TALLAHASSEE, FLORIDA

INGO W. STOLZ
GERARD R. DOBSON
RAYMOND K. SHELIN

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A RACEMIC COMPOUND OF α -HELICAL POLYPEPTIDE

Sir:

The existence of racemic mixtures, racemic solid solutions and racemic compounds of low molecular weight organic compounds in the solid state has been confirmed by various physical methods.¹ On the other hand, data pertaining to racemic interactions in liquid solutions have been inconclusive.²⁻⁵ We wish to present evidence that macromolecular compounds, the helical homopolypeptides of γ -methyl-D- and L-glutamate, form a definite racemic compound in solution as well as in the solid state.

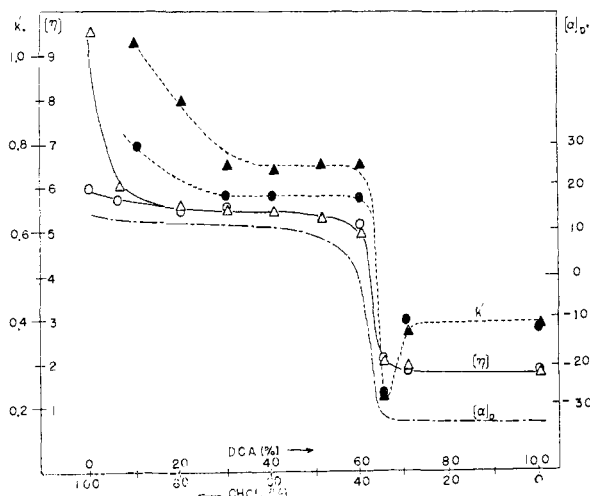


Fig. 1.—Dependence of Huggins' constant and intrinsic viscosity for L-PMG (DP = 1,700) and a mixture of L- and D-PMG (DP = 1,700) on solvent composition: —, $[\eta]$; - - - - -, k' ; \circ - and \bullet -, L-PMG; \triangle - and \blacktriangle -, 1:1 mixture of L- and D-PMG; semi-solid line represents $[\alpha]_D$ curve for L-isomer.

The behavior of a chloroform or a chloroform-dioxane solution of either α -helical poly- γ -methyl D- or L-glutamate (D- or L-PMG) was found to be remarkably different from that of a 1:1 mixture of the two enantiomorphs in the same solution. When chloroform-dioxane (2:1 by volume) solutions of D- and L-PMG (each 8.5 g./100 ml., DP = 2,900) were mixed at 37° , the resulting mixture changed into a rigid gel accompanied by a slight phase separation. The phenomenon was much more straight-

forward when a dimethylformamide (DMF) solution, in which the polypeptide chain exists also as an α -helix, was employed. Blending the enantiomorphous PMG solutions in DMF (1 g./100 ml., DP = 1,700) at 100° resulted in immediate precipitation of a white polymeric material lacking optical activity. Moreover, blending of DMF solutions of D- and L-PMG (DP = 1,700) in different proportions at 100° gave similar precipitates, the weights and optical rotations of which were compared with those of the PMG which remained in solution (Table I). Irrespective of the proportions in which the two enantiomorphous polypeptides were mixed, the weight of the precipitate was twice that of the lesser component.

TABLE I

COMPARISON OF WEIGHTS AND SPECIFIC OPTICAL ROTATIONS FOR THE PRECIPITATE AND PMG REMAINING IN LIQUID PHASE UPON BLENDING DMF SOLUTIONS OF D- AND L-PMG IN DIFFERENT PROPORTIONS

Initial ratio	D-PMG	1	3	1
	L-PMG	1	1	5
Initial wt., g.	D-PMG	1.000	1.667	0.201
	L-PMG	1.000	0.566	1.001
Precipitate ^a	Wt., g.	1.980	1.002	0.405
	$[\alpha]^{30}_D$	0.00	-0.51	0.00
PMG left in liq. ^b	Wt., g.	0	0.947	0.693
	$[\alpha]^{30}_D$..	-7.84	+9.32

^a Optical rotations were measured in dichloroacetic acid-chloroform (1:4 by volume, $c = 1.6$). ^b The remaining polymer was completely precipitated from the solution by addition of a large amount of water and dried, then measurements were carried out in the same solvent system.

The precipitate showed in the solid state and in chloroform solution the same infrared absorption bands (amide I at 1650 cm.^{-1} and amide II at 1545 cm.^{-1}) characteristic of α -helix as was observed on either enantiomorph. These results, together with the fact that the polypeptide modification obtained is less soluble than either enantiomorph, indicate that the precipitated material is a 1:1 mixture of α -helical D- and L-PMG, which reasonably may be called a "racemic compound" as in the case of monomeric compounds.

In order to ascertain whether this modification remains a racemic compound in solution or dissociates to the original components, viscosity measurements and estimates of the Huggins constant k' in the expression: $\eta_{sp}/c = [\eta] + k'[\eta]^2c$, where η_{sp} , c and $[\eta]$ are specific viscosity, concentration and intrinsic viscosity, respectively, were made at various compositions of the coil-producing solvent dichloroacetic acid (DCA) and the helix-forming chloroform (Fig. 1). The results are: (1) $[\eta]$ and k' values for both optically active and racemic PMG are related to molecular configuration as measured by optical rotation of the active form. Abrupt change in all of these properties takes place at 60 volume % DCA, where the helix-coil transition of PMG occurs. (2) Both active and racemic PMG show much higher $[\eta]$ and k' values in the helical region (up to 60 % DCA) than those in the coil region (above 60 % DCA).⁷ This would be due to associa-

(1) H. Gilman, "Organic Chemistry," Vol. I, 2nd ed., John Wiley and Sons, New York, N. Y., 1948, p. 248.

(2) R. Anschütz, *Liebigs Ann. Chem.*, **247**, 111 (1888).

(3) P. Frankland and R. H. Piccard, *J. Chem. Soc.*, **69**, 123 (1896).

(4) A. Cotton, *Ann. Chim. (Paris)*, [7] **8**, 347 (1896).

(5) A. Byk, *Ber.*, **37**, 4696 (1904).

(6) In this solvent the optically active PMG is an α -helix; see Fig. 1.
(7) G. E. Perlmann and E. Katchalski, *J. Am. Chem. Soc.*, **84**, 452 (1962).