the $\beta$-configuration in the solid state were prepared by initiating with hexylammonium hydroxide to very low DP. We take as an example PBG prepared by initiating to DP 5.2. Solid films cast from different solvents show a single C=O amide frequency at 1628 ± 2 cm.$^{-1}$ characteristic of the $\beta$-form.[2] In solution, however, an additional C=O band is observed at 1658 cm.$^{-1}$ (chloroform), 1670 cm.$^{-1}$ (dioxane). This band appears to be associated with a solvated form since its frequency is solvent dependent. Both the 1628 and the higher frequency band appear at high concentrations ($\sim$20%) but upon dilution the 1628 band becomes progressively weaker until at 0.5% concentration only the higher frequency C=O band remains. The specific rotation in chloroform changes continuously with concentration from +18 at 5% to +2 at 0.75%, but in DCA shows a constant value of −14. The intrinsic viscosity is low: $[\eta]_{\text{DCA}} = 0.056$.

The following conclusions may be drawn from these observations. (1) The $\alpha$-helical configuration is the stable form of high molecular weight poly-$\gamma$-benzyl-L-glutamate dissolved in weakly interacting solvents such as chloroform. (2) In strongly interacting solvents such as dichloroacetic acid the configuration is that of a randomly coiled polymer: this is presumably due to strong solvation and is independent of molecular weight. (3) With very low molecular weight polymers in weakly interacting solvents, however, two forms exist. One of these is believed to be a solvated form because of the solvent dependence of the C=O amide frequency. The other form is the intermolecularly bonded $\beta$-form which upon dilution is converted to the solvated form.

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## THE CATALYTIC DECOMPOSITION OF HYDROGEN PEROXIDE SOLUTIONS BY COMPLEX METAL AMMINES ADSORBED ON SILICA GEL

*Sir:*

The catalytic effect of cobalt and nickel sulfate adsorbed on the surface of silica gel upon the decomposition of a hydrogen peroxide solution has been reported to be only slight.[1]

Some of our recent work revealed that the complex metal amines of cobalt(II), copper(II), or nickel(II) adsorbed on the surface of iron-free silica gel very effectively catalyzed the decomposition of hydrogen peroxide solutions. When 1 g. of silica gel with its adsorbed metal ammine was placed in contact with 25 ml. of a 3% hydrogen peroxide solution, with or without its preservative, the decomposition was complete in 15 minutes at room temperature. A steady evolution of oxygen could be observed.

The complex metal ammines of silver(I), zinc(II), cadmium(II), or cobalt(III) adsorbed on the surface of silica gel failed to catalyze the decomposition of hydrogen peroxide solutions. Ammonia itself adsorbed on the surface of silica gel failed to effect any observable decomposition. It is of special interest to note that only those metal ammines characterized by unpaired electrons, hence paramagnetic, effected the decomposition of hydrogen peroxide solutions.

The adsorbed metal ammines that catalyzed the decomposition did not lose their activity with use. Samples of each were used on a fresh 3% hydrogen peroxide solution daily for a period of one month and were as active at the end of that period of time as they were at the beginning. The amount of the metal ammines adsorbed ranged from one to two millimoles per gram of silica gel. The metal ammines were prepared from metal nitrate solutions and concentrated ammonium hydroxide.[2]

Aqueous solutions of the nitrates of copper(II), cobalt(II) and nickel(II) produced little or no decomposition of 3% hydrogen peroxide, nor did aqueous ammonia solution itself. However, aqueous solutions of the complex ammines of copper(II), cobalt(II) and nickel(II) did produce rapid decomposition of the peroxide.

The same metal ions—cobalt, copper, nickel, silver, zinc and cadmium—coördinated with ethylenediamine or diethylenetriamine and adsorbed on the surface of silica gel, failed to give any noticeable catalytic decomposition of hydrogen peroxide solutions. Steric considerations and the stronger bonding of the metal ion to the ligand in these series may make it difficult for contact to be established between the hydrogen peroxide and the central metal ions of the adsorbed entity. The adsorption in these series ranged from 0.5 to 1.5 millimoles per gram of silica gel.

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[1] L. A. Nickolaw and Kobazeo, *J. Phys. Chem. U.S.S.R.*, **20**, 145–150 (1946).

[2] G. W. Smith, *J. Phys. Chem.*, **43**, 638 (1939).

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## THE SYNTHESIS OF TERTIARY NITROPARAFFINS[1]

*Sir:*

While tertiary nitroparaffins have been known for a long time they have in no case been obtained by reactions which can be regarded as useful preparative methods.[2] We wish to describe the first practical synthesis of *t*-nitroparaffins, namely, the oxidation of *t*-carbinamines, $RR'R''C\text{-}NH_2$, to

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[2] In liquid phase nitrations, small amounts of hydrocarbon are heated with dilute nitric acid (generally around 130–150°) in sealed tubes which have to be opened for "periodic relief of pressure." Large numbers of sealed tubes are required, complex mixtures are produced, and the yields of *t*-nitrocompounds are poor [see, *e.g.*, S. S. Nametkin and K. S. Zabrodina, *Doklady Akad. Nauk S.S.S.R.*, **75**, 395 (1950); *C.A.*, **45**, 6998 (1951)]. Despite its great commercial importance, Hass' vapor phase nitration process can hardly be regarded as a laboratory synthesis, the more so since it gives rise to complex mixtures. And the reaction of silver nitrite with *t*-alkyl halides gives 0 to 5% yields of *t*-nitro compounds, B. Taub, Ph.D. Thesis, Purdue University, 1952.