and the outer two lines become difficult to observe. As the temperature is decreased, the line widths continue to increase, and it ultimately becomes impossible to observe the outer two lines; hence the spectrum appears to consist of five lines. As the line width increases in magnitude relative to the line separation, one also finds that the observed relative intensities of the spectral lines change from 1:6:15:20:15:6:1 to 1:4:6:4:1. This is a general phenomenon and has been very well demonstrated by Lebeder, *et al.*,[10] by means of detailed calculation of the spectral patterns to be expected as one allows the line width to increase relative to the line separation.

Finally, samples containing 10^{-1}–10^{-3} *M* adamantane have been studied. At the higher concentrations, spectra identical with that of benzene anion radical were observed, *i.e.*, seven lines, $a_{\mathrm{H}} = 3.80$ (± 0.01) oersteds and $g = 2.00277$ (± 0.00005) between −110 and −120°. Upon lowering the temperature below the freezing point of the solvent, spectra such as those shown in Figures 2 and 3 were obtained. In the more dilute samples, a seven-line pattern (sometimes a five-line spectrum with an intensity distribution expected for seven lines) was observed with $a_{\mathrm{H}} \sim 3.90$–4.00 oersteds and $g = 2.0027$ (± 0.0001) at ~−125°. Some of the latter solutions may have been frozen. Lowering the temperature beyond −125° gave results similar to those shown in Figures 2 and 3. Qualitatively, the dilute samples gave less intense spectra by at least an order of magnitude than that used to record Figure 3.

There is no doubt that the above spectra could be derived from benzene present as a contaminant in the adamantane. Benzene concentrations as low as one part in 10^7 on a mole-to-mole basis can probably be detected in a 10^{-1} *M* solution of adamantane.[11] It is estimated from esr and ultraviolet measurements that the benzene concentration in the adamantane samples studied was approximately two orders of magnitude greater than this minimum value. The adamantane was purified by two sublimations, the first at atmospheric pressure and the second under high vacuum conditions.

The possibility also exists that benzene is derived from adamantane itself by reaction with sodium–potassium alloy. A distinction between these two possibilities could be made by an independent determination of the amount of benzene present in samples of adamantane. Such a determination might be possible through the use of isotopic dilution techniques.[12]

After consideration of the above evidence one concludes the parameters reported by Bowers, *et al.*,[1] for adamantane anion radical, *i.e.*, five broad lines (~2 oersteds in width), of relative amplitudes approximately given by the binomial distribution expected for five lines (1:4:6:4:1), hyperfine splitting $a_{\mathrm{H}} = 3.90$ oersteds and $g = 2.0029$ at −150° in a 2:1 mixture of THF and DME, could equally well have been those of the benzene anion radical under rigid solution conditions.

Acknowledgment. Helpful correspondence and conversations with Professors K. W. Bowers and F. D. Greene and the long and continued interest of Dr. T. L. Cairns are acknowledged.

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(10) Ya. S. Lebeder, D. M. Chernikova, N. N. Tekhomirova, and V. V. Voevodskii, "Atlas of Electron Spin Resonance Spectra," Consultants Bureau, New York, N. Y., 1963.

(11) The extreme sensitivity of esr should be noted. It is obvious from Figure 3, where the benzene concentration is between 10^{-5} and 10^{-6} *M*, that a 10- to 100- dilution would still yield an observable esr spectrum (with appropriate changes in spectrometer parameters). This corresponds to 10^{-11} or 10^{-12} mole of benzene anion radical for a sample of 0.1 ml. This is within the nominally quoted esr spectrometer sensitivity.

(12) This experiment was suggested by Professor C. Gardner Swain.

Stereoregular Modes of Double Bond Opening Determined in the Initial Short Period of the Anionic Polymerization of Isopropyl Acrylate

Sir:

We report in this communication that in the anionic polymerization of isopropyl acrylate initiated with phenylmagnesium bromide or diphenylmagnesium: (a) different modes of monomer double bond opening, *i.e.*, the *cis* mode,[1] the *trans* mode, and a 1:1 mixture of them, occur in different temperature ranges separated by narrow boundary regions, (b) the opening mode is determined in the initial very short period, and (c) the initially determined mode persists against temperature change beyond the boundary of its characteristic range.

It was reported previously[2] that when isopropyl acrylate-α,β-d_2 with the ratio, γ, of the α,*trans*-β-d_2 to the α,*cis*-β-d_2 isomer equal to 5 is polymerized in toluene at −78° using phenylmagnesium bromide as catalyst, two diisotactic processes with *cis* and *trans* opening of the double bond take place in the polymerization to give a polymer with $\kappa \approx 1$. Here κ is the intensity ratio of the lower to the higher field nmr signal of the *meso*-methylene protons, and $\kappa = \gamma$ and $\kappa = 1/\gamma$ mean *trans* and *cis* opening of the double bond, respectively, according to the assignment of the two *meso*-methylene signals.[3] It was found, however, that polymerization in toluene[4] at −57.5° or higher temperatures (confirmed up to 0°) gives a polymer with $\kappa \approx \gamma$, while polymerization at −62.5° or lower temperatures (confirmed down to −83°) gives a polymer with $\kappa \approx 1$. When ethyl ether was used as solvent, polymers with $\kappa \approx \gamma$ and $\kappa \approx 1$ were obtained in the polymerizations at temperatures above −63° and below −73°, respectively.

When polymerization was performed in toluene or ether at 0° for an initial 30 sec and then at −83° for a succeeding 6 hr, a polymer with $\kappa \approx \gamma$ (Figure 1) was obtained, the same as in the polymerization at 0° throughout. The polymer may be regarded as mostly formed at −83°, because the temperature reached −60° and −83 ± 0.5° within 20 and 80 sec, respectively, and because only a small amount of polymer was obtained by polymerization for 1 min at 0°. *trans* opening of the double bond in the polymerization at −83° after the rapid fall of temperature from 0°

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(1) Was not confirmed for the Grignard-initiated polymerization.

(2) T. Yoshino and K. Kuno, *J. Am. Chem. Soc.*, **87**, 4404 (1965).

(3) T. Yoshino, M. Shinomiya, and J. Komiyama, *ibid.*, **87**, 387 (1965).

(4) Contains ether (5% in volume) from the Grignard solution.

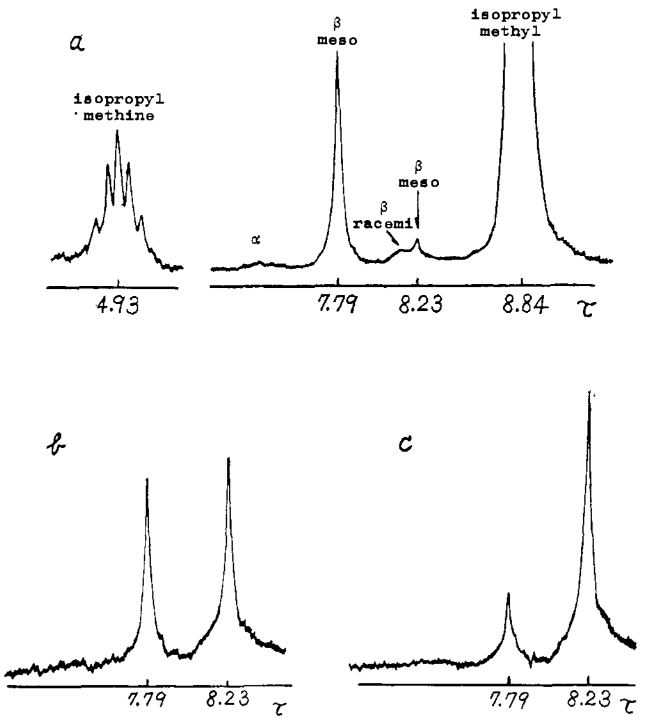

Figure 1. Nmr spectra of polyisopropyl acrylate-α,β-d_2 with $\kappa \approx \gamma$, $\kappa \approx 1$, and $\kappa \approx 1/\gamma$ prepared from monomer with $\gamma \approx 5$ by anionic processes (a) with PhMgBr in toluene at 0° for initial 30 sec and then at $-83°$ for succeeding 6 hr, (b) with PhMgBr in toluene at $-83°$ for initial 4 min and then at $-57.5°$ for succeeding 6 hr and (c) with Ph_2Mg in toluene at $-83°$ for 6 hr. The spectra were measured on 10% solutions in benzene at room temperature by a Varian HR-100 spectrometer. The spectra of the other polymers mentioned in this communication are not shown, because they are practically the same as those shown above.

and in the polymerization at 0° throughout is, therefore, regarded as determined within the initial 1 min prior to substantial formation of polymer. We see also that the initially determined mode is not altered by a rapid fall of temperature far beyond the boundary near $-60°$.

When polymerization was performed in toluene at $-83°$ for an initial period of 4 min and then at $-57.5°$ (attained in 1 min) for 6 hr, a polymer with $\kappa \approx 1$ (Figure 1) was obtained, although polymerization at $-83°$ for an initial 4 min and at 0° for 6 hr following gave a polymer with $\kappa \approx \gamma$. We see, therefore, that *cis* opening of the double bond, as well as *trans* opening, is determined within the initial 5 min, and that the initially determined mode with *cis*/*trans* ≈ 1 persists against rise of temperature slightly above the boundary.

Because of the complex nature of the Grignard reagent,[5] the observed persistence of the initially determined mode might be supposed to be caused by a delay of change with temperature in the phenyl Grignard *alone*. The following experiments show, however, that this is not the case, at least for the rapid fall of temperature from 0 to $-83°$. Toluene solutions of phenylmagnesium bromide and monomer maintained at 0° (or at $-83°$) were rapidly cooled to $-83°$ (or heated to $-57.5°$) and then mixed after 1 min (or 8 min) from the beginning of the rapid temperature change. The polymerizations at -83 and $-57.5°$ gave polymers with $\kappa \approx 1$ and $\kappa \approx \gamma$, respectively.

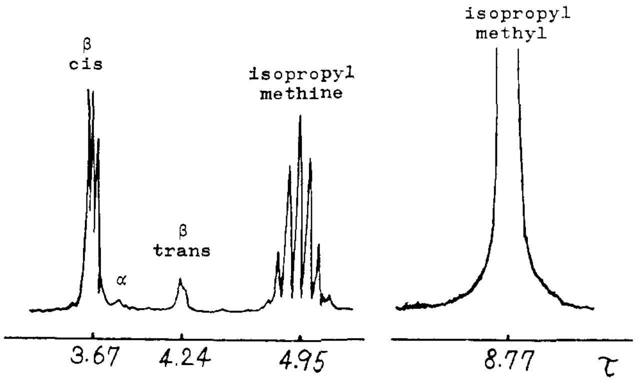

Figure 2. Nmr spectrum of isopropyl acrylate-α,β-d_2 with $\gamma \approx 5$.

When diphenylmagnesium was employed as catalyst, polymerization in toluene[6] gave a polymer with $\kappa \approx \gamma$, $\kappa \approx 1/\gamma$ (Figure 1), or $\kappa \approx 1$, depending on whether the temperature, fixed throughout the course of polymerization, was above $-13°$, below $-68°$, or between -20 and $-62°$. Polymerization carried out at 0° for an initial 30 sec and then at $-83°$ for succeeding 6 hr, however, gave a polymer with $\kappa \approx \gamma$, while polymerization performed at $-30°$ for an initial 30 sec and then at $-83°$ for the succeeding 6 hr gave a polymer with $\kappa \approx 1$. Therefore, the persistence of the initially determined mode is not limited to the Grignard initiated polymerizations.

Isopropyl acrylate-α,β-d_2 with $\gamma \approx 5$ (Figure 2) was prepared by the method described previously[7] for methyl acrylate-α,β-d_2 with $\gamma \approx 3$, except that heavy hydrogen was added at $-20°$ (20° previously).

Phenylmagnesium bromide in ether (1.61 mole/l.) was prepared by the usual method without using any initiator. The Br/Ph ratio was found to be 1.00 ± 0.01 by acid titration for basic magnesium and Mohr's method for bromine. Diphenylmagnesium was prepared from an ethereal solution of phenylmagnesium bromide and dioxane mainly according to the method of Salinger and Mosher[8] (except purification by recrystallization from ether at $-40°$). The dioxane/Ph ratio and the Br/Ph ratio were found to be 0.024 (by gas chromatography) and 0.0058, respectively.

Polymerization was carried out in a glass apparatus composed of two flasks A and B combined to form a single neck stopped with a silicon rubber plug. Solvent was introduced by means of a syringe into A and B (2.2 ml in each) of the apparatus filled with argon. A catalyst solution and monomer (0.5 ml) were added to the solvents in A and B, respectively. The molar ratios of PhMgBr and Ph_2Mg to monomer were 1:10 and 1:20, respectively. The polymerization apparatus was placed in an ice-water bath (0°), a Dry Ice-acetone bath $(-83 \pm 2°)$, or an acetone bath $(-5\sim-78°)$ which was regulated at a specified temperature with accuracy of $\pm 0.5°$ by using glass tubes filled with Dry Ice-ethyl ether mixtures and an electric heater. After the contents attained thermal equilib-

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(5) D. O. Cowan, J. Hsu, and J. D. Roberts, *J. Org. Chem.*, **29**, 3688 (1964), and papers cited therein.

(6) Contains ether (2% in volume) from the catalyst in an equivolume mixture of ether and toluene (1.00 mole/l.).

(7) T. Yoshino, J. Komiyama, and M. Shinomiya, *J. Am. Chem. Soc.*, **86**, 4482 (1964).

(8) R. F. Salinger and H. S. Mosher, *ibid.*, **86**, 1782 (1964).

rium, the monomer solution in B was poured into A by inclining the apparatus. The polymerization temperature was changed rapidly, if required, by transferring the apparatus to another bath and shaking it vigorously. The temperature was recorded by means of a thermocouple inserted in another apparatus in the same condition.

After polymerization was stopped by adding methanol, polymer was precipitated with petroleum ether, dissolved in acetone, precipitated again with 8% hydrochloric acid, washed with water, and then dried under vacuum at 50° for 24 hr. The yield was about 60 and 80% in the low temperature polymerizations for 6 hr initiated with PhMgBr and Ph_2Mg, respectively. The yield decreased at higher temperatures.

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The Molecular Structure of a Peroxo-Bridged Dicobalt Cation

Sir:

There exists a large number of compounds containing two cobalt atoms connected by one, two, or three bridging groups. These bridging groups include hydroxo, amido, peroxo, and nitrito radicals; the remaining coordination sites on the cobalt atoms can be occupied by ammine groups, cyanide ions, or organic amines. The nature of the bonding in these bridged compounds, and especially in those containing peroxo and nitrito bridges, has been the subject of discussion since their discovery. We have now determined by single crystal X-ray diffraction techniques the structure of a sulfate of the cation $[(NH_3)_5CoO_2Co(NH_3)_5]^{+5}$.

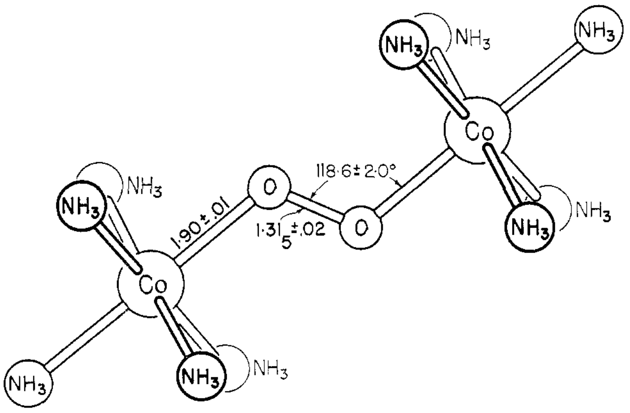

Figure 1. The geometry of the $[(NH_3)_5CoO_2Co(NH_3)_5]^{+5}$ cation.

The decaammine-μ-peroxodicobalt cation exists in an oxidized and a reduced form, the oxidized form (charge +5) being green and paramagnetic and the reduced form (charge +4) brown and diamagnetic. If the bridging group in the oxidized form is taken to be a peroxide ion, O_2^{-2}, then the cobalt atoms must have formal oxidation states +4 and +3 (or some other combination giving +7) to account for the +5 charge; alternatively, one can consider the bridging group to be a superoxide ion, O_2^-, and then both cobalt atoms can be in a more usual +3 oxidation state. Attempts have been made to decide between these two possibilities on the basis of the epr spectrum of the compound,[1] but these experiments have only demonstrated the equivalence of the cobalt atoms and have not provided information as to the distribution of electrons in the compound.

Goodman, Hecht, and Weil[2] have summarized these and other explanations and theories regarding the peroxo bridge in these types of compounds. The latest theoretical work is that of Vlček,[3] in which he considered the oxygen–oxygen bond to be perpendicular to the cobalt–cobalt axis; he presumed the bonding to be between d orbitals of the cobalt atoms and π electrons on the peroxo group, in analogy to the bonding in the platinum–olefin complexes. This structure was in fact subsequently reported by Vannerberg and Brosset[4] for the compound decaammine-μ-peroxodicobalt pentanitrate. However, their structure determination was based on only 234 observed reflections and the structure was refined only to an R factor of 19%; moreover, there was some question in their paper as to the correct space group, and they were forced to assume a disordered structure to obtain even the agreement they reported. Thus, their apparent confirmation of Vlček's structure is not reliable. Because of the unusual nature of the bonding postulated by Vlček and the importance of compounds such as this in constructing theories of bonding, we have examined the crystal structure of a different compound containing the same cation, decaammine-μ-peroxodicobalt monosulfate tris(bisulfate), $(NH_3)_5CoO_2Co(NH_3)_5SO_4(HSO_4)_3$. This is a new compound not previously reported; Vortmann[5] in his original paper on these compounds reported for the sulfate the formula $(NH_3)_5CoO_2Co(NH_3)_5(SO_4)_2HSO_4 \cdot 3H_2O$. This last compound forms when crystallization is from 1 F sulfuric acid; it is monoclinic and its structure is now under investigation in these laboratories.

The compound described here is obtained by crystallization from sulfuric acid more concentrated than about 2 F. It crystallizes in the orthorhombic space group $P2_12_12_1$ with unit cell dimensions a = 16.36, b = 13.95, and c = 9.98 A; there are four formula units in the cell. The structure was solved by Patterson methods and refined by three-dimensional least-squares methods based on 1458 reflections, with a final R factor of 0.077. Many features of this structure are of interest and these will be presented in detail elsewhere; the important information to be reported here is the molecular structure of the bridged peroxodicobalt cation, which is as shown in Figure 1. Each of the cobalt atoms is surrounded by five ammonia molecules and an oxygen atom of the bridging group. These are arranged at the corners of an almost regular octahedron, the cobalt–nitrogen distances all being 1.95 ±

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(1) I. Bernal, E. A. V. Ebsworth, and J. A. Weil, *Proc. Chem. Soc.*, 57 (1959).

(2) G. L. Goodman, H. G. Hecht, and J. A. Weil, "Free Radicals in Inorganic Chemistry," Advances in Chemistry Series, No. 36, American Chemical Society, Washington, D. C., 1962, p 90.

(3) A. A. Vlček, *Trans. Faraday Soc.*, **56**, 1137 (1960).

(4) N.-G. Vannerberg and C. Brosset, *Acta Cryst.*, **16**, 247 (1963).

(5) G. Vortmann, *Monatsh. Chem.*, **6**, 404 (1885).