succinic acid. In fact, the failure to observe it in the case of the reduction by Cr^{2+} or V^{2+} of the Co^{III} complex containing maleic acid as ligand[3] may prove to be a useful clue for the elucidation of the mechanism of the electron-transfer process. In this communication we report some observations on the isomerization. Data on the reduction are available.[4]

Figure 1 shows the fumaric acid produced in two reaction mixtures differing only in their perchloric acid content. Replacement of $HClO_4$ by HCl in a solution containing initially 0.0113 M V^{2+}, 0.156 M maleic acid, and 0.85 M H^+ did not affect the amount of fumaric acid obtained upon complete consumption of the V^{2+}. Included in Figure 1 is the V^{2+} consumption in the parallel reduction of maleic acid.[4] The isomerization is caused by V^{2+}; it does not take place if V^{2+} is not present, other conditions being constant. The other oxidation states of vanadium (V^{3+}, VO^{2+}) do not cause isomerization. The inverse, thermodynamically unfavorable, conversion of fumaric to maleic acid was not observed. Determination of fumaric acid in the presence of maleic and succinic acids was made polarographically under the conditions suggested by Warshowsky, et al.[5] The aliquots from the reaction mixture were exposed to air or mixed with a Fe^{3+} solution to stop the reaction and were analyzed polarographically after removing the metal ions on a Dowex 50 column. Fumaric acid, because of its limited solubility, is precipitated from reaction mixtures containing relatively high concentrations of maleic acid and was also identified by taking its melting point and ir spectrum. Analogous but slower isomerization with that of maleic acid is also observed with its derivative citraconic acid which is converted to mesaconic acid.

The study of the temperature dependence is made difficult because of the parallel oxidation of V^{2+} and the establishment upon mixing of a complex formation equilibrium between V^{2+} and the organic acids.[4] Nevertheless, it is mentioned that in two identical reaction mixtures containing 0.168 M maleic acid, 0.0113 M V^{2+}, and 0.058 M $HClO_4$ at 20 and 60° the percentage of fumaric acid formed over the initial maleic acid was 29.6 and 24.3, respectively. The determination was made after all the V^{2+} had been oxidized. Increase in temperature seems to favor reduction over isomerization.

In a preliminary attempt to follow more closely the isomerization and to find out what happens locally at the double bond, we did an experiment in deuterated water (50% D_2O) and determined by nmr the fraction of CD bonds in the fumaric acid produced. The mixture contained initially 0.25 M maleic acid, 0.05 M V^{2+}, and 0.1 M $HClO_4$. The fraction of CD bonds found in the fumaric acid which precipitated was 20–22%. Fumaric acid itself, without V^{2+}, does not undergo exchange. Figure 1 shows that formation of fumaric acid is faster at lower hydrogen ion concentration. Using the empirically determined[4] rate law and rate constant for the oxidation of V^{2+} and assuming first-order dependence of the isomerization on (V^{2+}), we can obtain from the data estimates of the rate constant for isomerization. We find then that the increased rate of production of fumaric
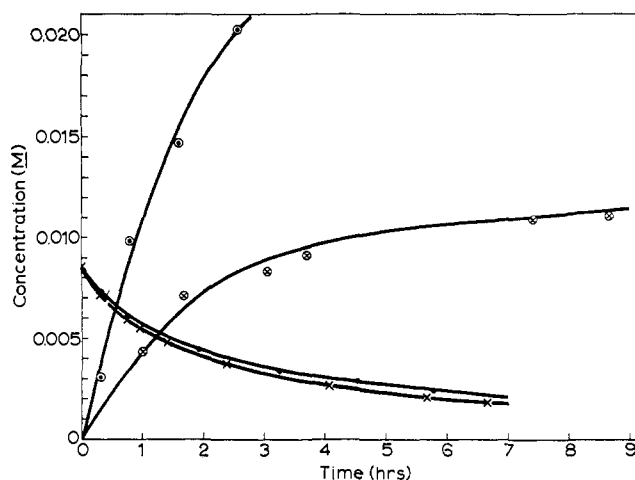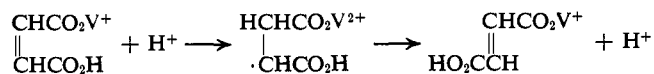
(4) E. Vrachnou-Astra, Ph.D. Thesis, submitted to the National Technical University, Athens, Greece.
(5) B. Warshowsky, P. J. Elving, and J. Mandel, Anal. Chem., 19, 161 (1947).

Figure 1. Isomerization of maleic acid by vanadous ion. Initial concentrations: $(V^{2+})_0$ = 0.009 M, (maleic acid)$_0$ = 0.156 M. ○ and ⊗ fumaric acid produced; and ● and ✕, the corresponding V^{2+} concentrations in 0.43 and 0.85 M $HClO_4$, respectively.

acid at lower acid is mainly due to an inverse dependence on (H^+) of the isomerization itself and to a lesser extent to the decreased rate of the competing oxidation of V^{2+}. In a qualitative way, this fact is illustrated in Figure 1 where it is seen that the curves of (V^{2+}) vs. time depend much less on acid than those of (FA) vs. time. The significance of this observation is that it provides a link between the isomerization and the complex formation equilibrium between V^{2+} and maleic acid.

The factors affecting exchange of the double-bond hydrogens and its relation to isomerization can best be illustrated with the aid of a specific reaction scheme

$$\underset{\overset{\|}{CHCO_2H}}{CHCO_2V^+} + H^+ \longrightarrow \underset{\cdot CHCO_2H}{HCHCO_2V^{2+}} \longrightarrow \underset{HO_2CCH}{\overset{CHCO_2V^+}{\|}} + H^+$$

If there is no labilization of the hydrogens in the intermediate, the statistically expected fraction of CD's in 50% D_2O is 12.5%. The fact that we observe more than this minimum indicates that the hydrogens of the intermediate become labile or that we have large isotopic discrimination, or that the first step in the above scheme is reversible. In addition, an analogous scheme for exchange can be written for the fumaric acid produced in the system. The evaluation of the relative importance of all these factors is the subject of further investigation.

E. Vrachnou-Astra, D. Katakis
Nuclear Research Center "Democritos"
Aghia Paraskevi Attikis, Athens, Greece
Received July 10, 1967

Stereospecific Reaction of Growing Ends of Polyacrylate Anions with Water, Hydrochloric Acid, and Acetic Acid

Sir:

A series of oligomers was prepared by adding H_2O, HCl, or CH_3COOH to a polymerization solution of isopropyl acrylate-α,β,β-d_3 in toluene after 2 min of
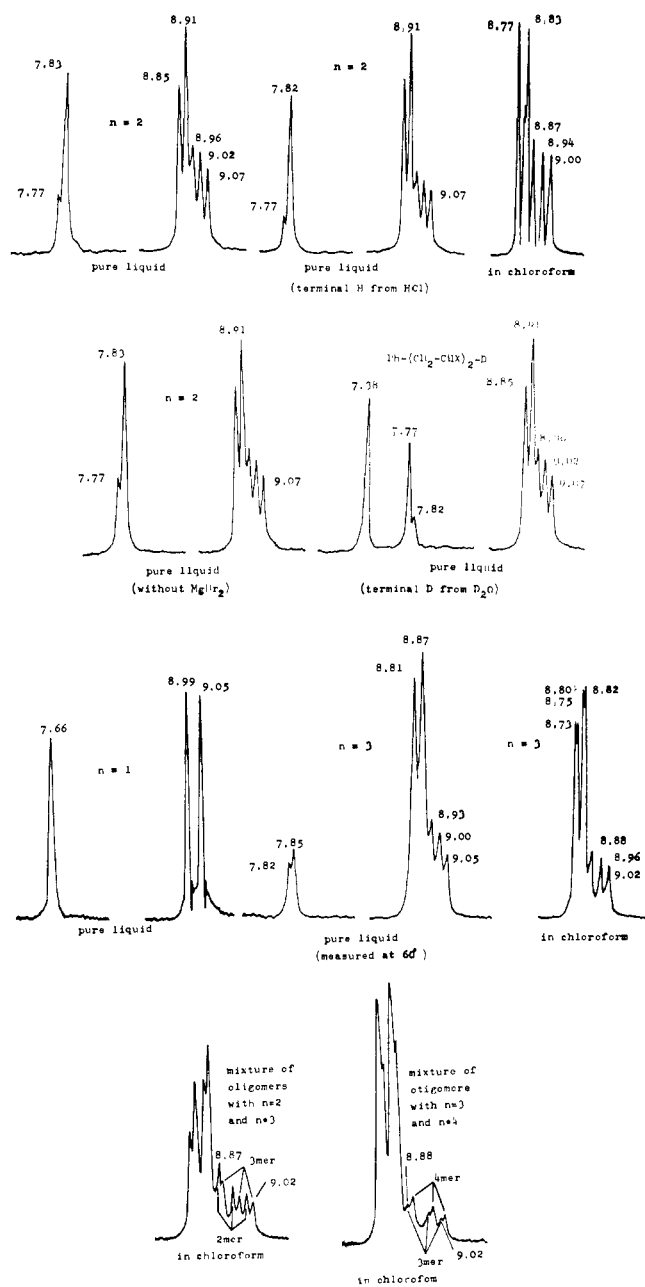
Figure 1. Backbone and ester methyl proton spectra of Ph(CD₂-CDX)ₙH and Ph(CD₂CHX)₂D. So far as not mentioned otherwise in the figure, the oligomers were prepared by adding H_2O to a mixture of PhMgBr, $MgBr_2$, $\alpha,\beta,\beta\text{-}d_3$ monomer, and toluene (1/1/3/10 in moles) at $-80°$, and the spectra were obtained at room temperature by a Varian HR-100 spectrometer. The concentrations of oligomers in $CHCl_3$ were 20%. The same spectra were obtained when CH_3COOH was used to interrupt polymerization.

polymerization reaction at $-80°$ initiated with PhMgBr. These oligomers were fractionated by vacuum distillation and each fraction was redistilled for further purification. Nmr inspection showed that the same series of oligomers was produced independent of whether H_2O, HCl, or CH_3COOH was used.

The oligomers are considered to have the structures represented by Ph(CD₂CDX)ₙH with isotactic α-methine configurations because oligomers from the $\alpha,\beta\text{-}d_2$ monomer were found previously[1] to have the structures represented by Ph(CHDCDX)ₙH or Ph(CHDCDX)ₙD

(1) T. Yoshino, J. Komiyama, and H. Iwanaga, *J. Am. Chem. Soc.*, in press.

and to have isotactic α-methine configurations. Here X represents the isopropyl ester group, and the terminal H (or D) represents the hydrogen (or deuterium) from H_2O (or D_2O), HCl, or CH_3COOH.

The number of mer units in each of these oligomers was found from the intensity ratio of the phenyl signal to the ester methine or ester methyl multiplet. The ester methyl groups of the first unit (of all oligomers other than the oligomer with $n = 1$) appear as a pair of doublets, being made nonequivalent by the adjacent phenyl group, while the ester methyl groups of the second or a later unit appear as a doublet. The positions of the components of these multiplets are slightly different between oligomers with $n = 2$, 3, and 4, as seen in Figure 1. By inspecting the ester methyl multiplet, the oligomers with $n = 2$ giving the spectra shown in Figure 1 were found to be free from the oligomer with $n = 3$, and the oligomer with $n = 3$ giving the spectrum shown in Figure 1 was found to contain less than 20% of the oligomers with $n = 2$ and 4.[2] The oligomers with $n = 2$ and 3 were found to be free from the oligomers with $n = 1$ by the absence of the α-proton signal of the latter at τ 7.66.

Two signals which are much different in intensity are found near τ 7.8 in the pure liquid spectrum of the oligomer with $n = 2$. The separation between these signals is larger in pure liquid than in $CHCl_3$ or CCl_4 solution. Both signals are assigned to the protons at different positions on the terminal α carbon, but neither of them is ascribable to impurity or other sources because the intensity ratio of these signals is reversed in the spectrum (in Figure 1) of the oligomer Ph(CD₂-CHX)₂D which was prepared by adding D_2O to a polymerization solution of the $\beta,\beta\text{-}d_2$ monomer. An intensity ratio far different from unity shows that the reaction of a living oligomer with H_2O, HCl, or CH_3COOH is stereospecific. The intensity ratio is considered to represent the lower limit of the stereospecificity of the reaction, because isomerization might have occurred at the terminal CHDX group in the course of the repeated distillations. It is found in Figure 1 that the stereospecific reaction with H_2O occurs in the polymerization solutions with and without $MgBr_2$.

Two signals are also found near τ 7.8 in the spectrum of the trimer Ph(CD₂CDX)₃H, and the intensity ratio of the lower to the higher field signal is smaller than unity, the same as in the spectrum of the dimer Ph-(CD₂CDX)₂H. However, the ratio is not as much different from unity as in the case of the dimer. This is considered to be due to coincidence in position of the lower field α signal of the trimer with the higher field α signal of the dimer and also to isomerization at the terminal CHDX group which is supposed to have occurred in the repeated distillations at high temperature (bath temperature 210~230°).

Isopropyl acrylate-$\alpha,\beta,\beta\text{-}d_3$ was prepared by D_2 addition to isopropyl propiolate-$\beta\text{-}d$.[1] Isopropyl acrylate-$\beta,\beta\text{-}d_2$ was prepared by D–H exchange at the α deuteron of acrylonitrile-$\alpha,\beta,\beta\text{-}d_3$ in H_2O to which was added CaO,[3] followed by hydrolysis and esterification.[4]

(2) Purity examination by using backbone proton signals, which was employed previously[1] for oligomers from the $\alpha,\beta\text{-}d_2$ monomer, is not applicable here because the signals of the terminal α-protons of the d_3 oligomers with $n \geq 2$ appear at nearly the same τ values.
(3) L. C. Leitch, *Can. J. Chem.*, **35**, 345 (1957).
(4) C. E. Brockway, U. S. Patent 2,666,782; *Chem. Abstr.*, **49**, 1780 (1955).

Acrylonitrile-α,β,β-d_3 was prepared by adding D_2 to propargylnitrile-β-d (98% D) which was obtained from nitrile-d_0 by repeating (eight times) H–D exchange with D_2O. The exchange was performed by shaking the mixture vigorously at room temperature for 8 hr without using any additives. Preparation of the oligomers and purification were performed by methods similar to those described previously.[1]

Tsuneo Yoshino, Hikaru Iwanaga, Kiyoshi Kuno

Basic Research Laboratories, Toyo Rayon Company
Kamakura, Kanagawa, Japan
Received September 18, 1967

The Effect of Polar Substituents upon ^{13}C–^{13}C Coupling Constants

Sir:

It is generally accepted that bond hybridization[1-8] plays an important role in the directly bonded ^{13}C–H spin–spin coupling constant. Nevertheless, charge polarization features[9] and variations in the carbon–hydrogen bond distance[10] have also been shown to alter the hyperfine contact interaction term important in the ^{13}C–H coupling mechanism. Thus, hybridizational arguments based on $J_{^{13}C-H}$ values may be used only with care on systems in which other electronic features remain essentially constant.

While the work of Frei and Bernstein[11] and of Lynden-Bell and Sheppard[12] has exhibited the importance of hybridizational variations in the ^{13}C–^{13}C coupling constant, the relative influence of polarizing groups has not been explored systematically for this particular coupling constant in a class of related compounds. Table I contains $J_{^{13}C-^{13}C}$ values[13] for a set of

Table I. The Effect of Polar Groups on Directly Bonded Coupling Constants

X	$J_{^{13}C-^{13}C}$, cps, in XC(CH$_3$)$_3$	$J_{^{13}C-H}$, cps, in XCH$_3$[a]
CH$_3$	36.9	126
NH$_2$	37.1	133
OH	39.5	141
Cl	40.0	150
Br	40.2	152

[a] N. Muller and D. E. Pritchard, *J. Chem. Phys.*, **31**, 1471 (1959).

compounds having very similar structures (*i.e.*, neopentane and related t-butyl derivatives), along with

(1) J. N. Shoolery, *J. Chem. Phys.*, **31**, 1427 (1959).
(2) N. Muller and D. E. Pritchard, *ibid.*, **31**, 768, 1471 (1959).
(3) M. Karplus and D. M. Grant, *Proc. Natl. Acad. Sci. U. S.*, **45**, 1269 (1959).
(4) N. Muller, *J. Chem. Phys.*, **36**, 359 (1962); **42**, 4309 (1965).
(5) H. S. Gutowsky and C. S. Juan, *J. Am. Chem. Soc.*, **84**, 307 (1962).
(6) C. Juan and H. S. Gutowsky, *J. Chem. Phys.*, **37**, 2198 (1962).
(7) H. Dreeskamp and E. Sackmann, *Z. Physik. Chem.* (Frankfurt), **34**, 273 (1962).
(8) J. H. Goldstein and R. T. Hobgood, Jr., *J. Chem. Phys.*, **40**, 3592 (1964).
(9) D. M. Grant and W. M. Litchman, *J. Am. Chem. Soc.*, **87**, 3994 (1965).
(10) D. S. Bartow and J. W. Richardson, *J. Chem. Phys.*, **42**, 4018 (1965).
(11) K. Frei and H. J. Bernstein, *ibid.*, **38**, 1216 (1963).
(12) R. M. Lynden-Bell and N. Sheppard, *Proc. Roy. Soc.* (London), **A269**, 385 (1962).
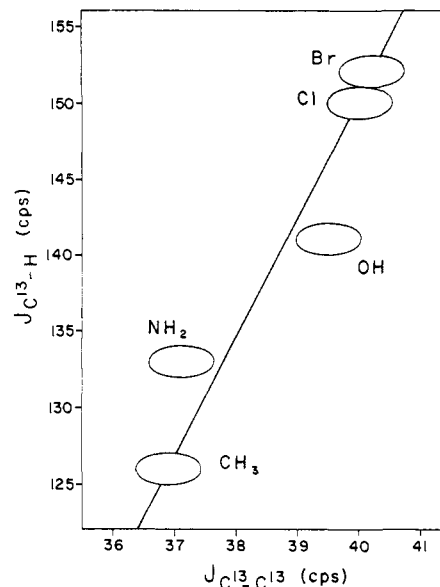(13) The measurement of these values was first reported in *Chem. Eng. News*, **45**, 46 (March 27, 1967).

Figure 1. The values of $J_{^{13}C-H}$ in X–CH$_3$ are plotted *vs.* $J_{^{13}C-^{13}C}$ in the similar X–C(CH)$_3$ compounds for X equal to CH$_3$, NH$_2$, OH, Cl, and Br.

values of $J_{^{13}C-H}$ obtained in the corresponding methyl compounds. It is to be noted from Figure 1 that both coupling constants increase in a directly proportional manner, although it should be stressed that the relative increase (25:125) in $J_{^{13}C-H}$ is more than twice that (3:37) noted in $J_{^{13}C-^{13}C}$. As both of these couplings have the same relative sign[14] and are affected in a similar manner by hybridizational and charge polarization features, it is reasonable to conclude that the important coupling mechanism must be similar in both instances. It is interesting, therefore, to speculate on the reason for the relative increases being different in the two cases. One is led to conclude that the electronic structure of both nuclei involved in the coupling is affected by the electronegative substituent and not merely the carbon atom which is directly bonded to the polar group. Otherwise, the two couplings would be expected to increase by the same relative amount. This conclusion suggests that the relatively simple calculations of $J_{^{13}C-H}$ values by Grant and Litchman[15] should be extended to include possible polarization changes in the effective nuclear charge of the directly bonded hydrogen atom. As a hydrogen is a terminal atom, inductive effects cannot be transferred onto additional atoms as they can in a methyl group. Thus, polarization effects due to an electronegative group can be expected to be less severe in an adjacent C–C bond when compared with an adjacent C–H bond, and $J_{^{13}C-^{13}C}$ can reasonably be expected to be less sensitive to directly attached polar substituents than is $J_{^{13}C-H}$.

The reduced sensitivity of $J_{^{13}C-^{13}C}$ to charge polarization effects is fortunate in one respect as even greater confidence can be placed in the use of $J_{^{13}C-^{13}C}$ values as a criterion for bond hybridization.[11,12] This conclusion is especially significant in the recent $J_{^{13}C-^{13}C}$ work of

(14) D. M. Grant, *J. Am. Chem. Soc.*, **89**, 2228 (1967).
(15) See ref 9. While this extension in the previous calculation may yield different numerical results, the central concept of ref 9, that the effective nuclear charge of the carbon is altered by polar groups, is merely extended to include both the carbon and hydrogen atoms.