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Transition Metal Catalysts. VII. Identification of the Active Site in Organometallic Mixed Catalysts by Copolymerization Kinetic Studies

BY FREDERICK J. KAROL AND WAYNE L. CARRICK[1]

Copolymerization of ethylene and propylene with different metal alkyls (CH_3TiCl_3, AlR_3, $(C_6H_5)_2Zn$, R_2Zn, etc.) in combination with a common transition metal compound (VCl_4) gave the same reactivity ratios in all cases, while copolymerization with a common metal alkyl (AlR_3) in combination with different transition metal compounds ($VOCl_3$, VCl_4, $TiCl_4$, $ZrCl_4$, $HfCl_4$) gave different reactivity ratios in every case. Since a change in the transition metal compound changed the nature of the active site but a change in the reducing agent did not, the growing polymer molecule must be attached to the transition metal center. In some of these catalysts, more than one active species is present with each site producing its own characteristic copolymer, and the resulting gross product is then a blend of several molecular species. These data are interpreted as support for a previously proposed propagation mechanism, and the effect of changes in the polarity of the active site is discussed.

Introduction

In copolymerization, there is competition between the different monomers for reaction at the same active polymer chain end; therefore, by systematically changing the monomer structure and/or the nature of the chain end, it is possible to determine the relative effect of steric and electrical factors on the propagation reaction. The fact that a styrene-methyl methacrylate mixture yields polymers of vastly different composition when polymerization is effected by reagents yielding radicals, carbonium ions or carbanions has served as a classic test for distinguishing these various propagation mechanisms.[2] In the newer Ziegler-type catalysts, there is considerable evidence that the propagation is of yet a fourth type,[3] and the classic test is not useful because methyl methacrylate is not readily polymerizable with most of these catalysts.

In the present work the technique of varying the cocatalyst composition (reducing agent + transition metal compound) and measuring changes in the copolymers produced from a given pair of monomers was used to identify the active catalyst site in a complex chemical system and to define several important features of the catalytic process. This paper extends the initial results presented in our earlier communication.[4]

Experimental

Polymerization Conditions.—Premixed cylinders of ethylene and propylene were prepared and analyzed by vapor chromatography using an activated alumina column. The chromatographic elution areas were multiplied by the factors 1.022 for ethylene and 0.854 for propylene to convert from the measured area per cent. to mole per cent. The gases used here contained 3–5% methane and ethane, which are inert under the polymerization conditions, ~0.5% carbon dioxide and traces of air (200–600 p.p.m.). (The role of oxygen is described by G. W. Phillips & W. L. Carrick, *J. Polymer Sci.*, in press.) Removal of carbon dioxide was effected by passage through "Linde" Molecular Sieves. The reactor was a 2 liter glass bowl equipped with a high-speed agitator (2400 r.p.m.), which was charged with 1100 ml. of cyclohexane, heated to 70°, pressurized with monomer to 30 psig., and the catalyst was injected by way of

hypodermic syringes through a rubber puncture disc. In all cases (except Fig. 4) the concentration of reducing agent was 10–100 times that of the transition metal compound. The yield of polymer was regulated by the amount of catalyst added. At the higher yields the heat of reaction caused the temperature to rise a few degrees. At the end of the experiment, the copolymer solution was blown out of the reactor by nitrogen pressure, coagulated in 2-propanol; the polymer was removed by filtration, washed and dried.

The fact that the temperature was not held constant should not affect the reactivity ratios since the curves (Fig. 3) are extrapolated to zero conversion, and it was shown that a wide range of temperature does not affect the ethylene–propylene solubility ratio. In other cases the influence of a few degrees change in temperature on reactivity ratios was shown to be small.[5,6]

Analysis of the Copolymers.—The propylene content of the resin was determined by measuring the infrared absorption at 7.26 μ. For this calibration known mixtures of both amorphous and crystalline polypropylene in a linear polyethylene were prepared and the absorbance/mil at 7.26 μ determined with a Perkin–Elmer Model 21 Spectrophotometer using a film of the linear polyethylene in the reference beam to compensate the polyethylene absorption in the 7–9 μ region and also to compensate the methylene absorption in polypropylene. Copolymer analyses were performed similarly with a sample of very high molecular weight, linear, polyethylene in the reference beam, and the propylene content was calculated by comparing the absorbance at 7.26 μ with the calibration obtained above (Fig. 1,) or by the formula

Weight % propylene = 66.7 (Absorbance at 7.26 μ)

Reproducibility is ±5% on analyses done in triplicate. This method inherently assumes that the absorption coefficient of the methyl group in the copolymer is the same as in polypropylene, but the fact that the absorption coefficient is the same in both crystalline and amorphous polypropylene indicates that this assumption is reasonable.

Ethylene–Propylene Solubility Ratio.—The amount of gas required to fill the reactor was determined by filling the empty reactor to various pressures from tared cylinders of the two monomers. This procedure was repeated with 1100 ml. of cyclohexane in the reactor. From these data and knowledge of the total volume of the system, the weight of monomer dissolved at various pressures was calculated at 30° and 70°. The data are summarized on Fig. 2, where the pressure refers to actual monomer partial pressure. Propylene is 6.3 times as soluble as ethylene on a weight basis and 4.2 times as soluble on a mole basis at 70°. At 30° the absolute solubility of both monomers is much greater, but the ratio is the same.

Results

In the copolymerization of two monomers there are four separate propagation steps.[7] In the

(1) Address inquiries to this author.

(2) C. Walling, E. R. Briggs, W. Cummings and F. R. Mayo, *J. Am. Chem. Soc.*, **72**, 48 (1950).

(3) (a) W. L. Carrick, A. G. Chasar and J. J. Smith, *ibid.*, **82**, 5319 (1960); (b) G. L. Karapinka and W. L. Carrick, *J. Polymer Sci.*, in press.

(4) W. L. Carrick, F. J. Karol, G. L. Karapinka and J. J. Smith, *J. Am. Chem. Soc.*, **82**, 1502 (1960).

(5) J. D. Sutherland and J. P. McKenzie, *Ind. and Eng. Chem.*, **48**, 17 (1956).

(6) M. Imoto and K. Saotome, *J. Polymer Sci.*, **31**, 208 (1958).

(7) (a) F. R. Mayo and F. M. Lewis, *J. Am. Chem. Soc.*, **66**, 1594 (1944); (b) F. T. Wall, *ibid.*, **66**, 2050 (1944); (c) F. R. Mayo and C.
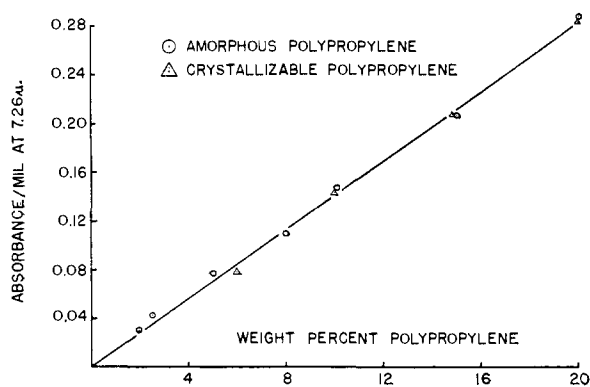
Fig. 1.—Calibration of infrared absorbance at 7.26μ in polypropylene–polyethylene mixtures.
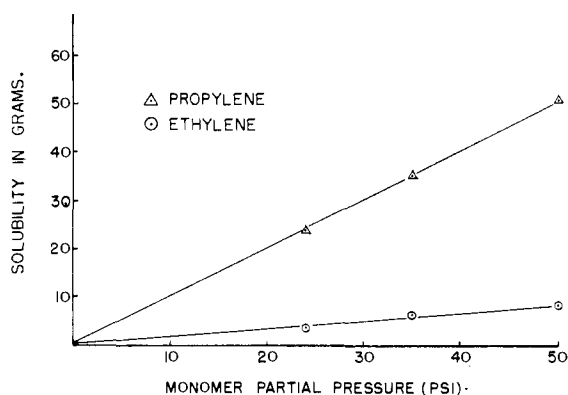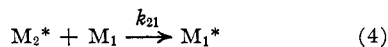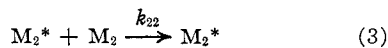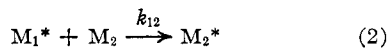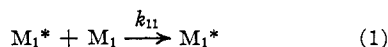

Fig. 2.—Solubility of ethylene and propylene in 1100 ml. of cyclohexane at 70°.

present case M_1 and M_2 refer to ethylene and propylene, respectively, and M_1^* and M_2^* refer to growing polymer molecules with ethylene (M_1^*) or propylene (M_2^*) residues at the active end.

$$M_1^* + M_1 \xrightarrow{k_{11}} M_1^* \tag{1}$$

$$M_1^* + M_2 \xrightarrow{k_{12}} M_2^* \tag{2}$$

$$M_2^* + M_2 \xrightarrow{k_{22}} M_2^* \tag{3}$$

$$M_2^* + M_1 \xrightarrow{k_{21}} M_1^* \tag{4}$$

Either monomer may add to either active end, and the relative reactivities are defined as $r_1 = k_{11}/k_{12}$ and $r_2 = k_{22}/k_{21}$. Under steady state conditions it may be shown that the instantaneous composition of the copolymer (dM_1/dM_2) formed from a given monomer mixture is

$$\frac{dM_1}{dM_2} = \frac{M_1}{M_2} \frac{r_1 M_1/M_2 + 1}{M_1/M_2 + r_2} \tag{5}$$

By substituting F for the mole ratio of the two monomers in solution (M_1/M_2) and f for the mole ratio of the two monomers in the first increment of copolymer, equation 5 may be rearranged to give[8]

$$\frac{F}{f}(f-1) = r_1 \frac{F^2}{f} - r_2 \tag{6}$$

Walling, Chem. Revs., 46, 191 (1950); (d) P. J. Flory, "Principles of Polymer Chemistry." Cornell University Press, Ithaca, New York, 1953, Chapter V.

(8) M. Fineman and S. D. Ross, J. Polymer Sci., 5, 259 (1950).
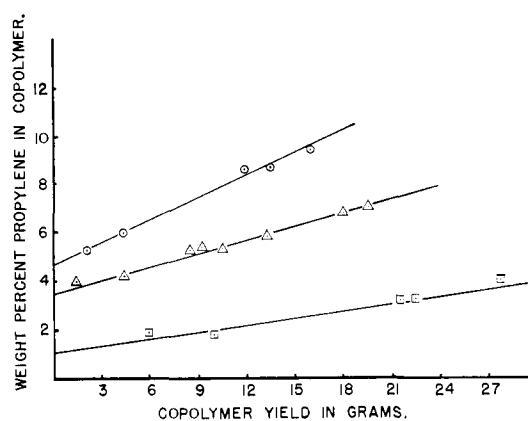
Fig. 3.—Copolymer composition vs. monomer composition: ⊙, 23.7 mole % propylene; △, 15.7 mole % propylene, ▣, 6.05 mole % propylene in the monomer mixture.
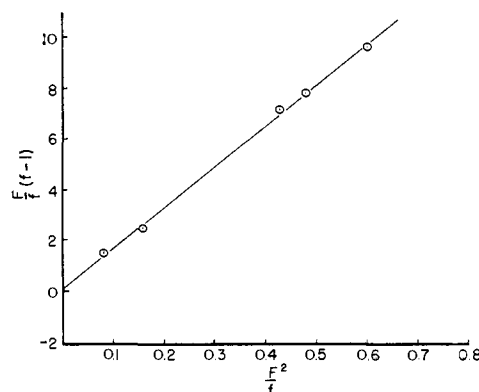
Fig. 4.—Fineman and Ross plot of the data of Table I to determine r_1 and r_2.

A plot of the left hand side of equation 6 against the coefficient of r_1 yields a straight line with r_1 as the slope and r_2 as the intercept.

In this work, copolymerizations were conducted by feeding a given composition of ethylene and propylene to a sealed reactor at a sufficient rate to maintain a pressure of 30 psig. The mole fractions of ethylene and propylene were calculated from analysis of the vapor space before polymerization and the known solubility ratio of propylene and ethylene (4.2:1). Since ethylene reacts faster than propylene and no monomer was vented, there was a progressive build-up of propylene in the reactor and in the copolymer, with increasing conversion. A plot of propylene content of the copolymer vs. yield of copolymer for a given monomer composition gave a family of straight lines (Fig. 3). The intercepts of these lines represent the composition of the first increment of copolymer formed from each monomer mixture and the mole ratio, f, was calculated from this instantaneous composition (Table I). Figure 4 shows a plot of these data for the $AlBr_3$–VCl_4–$Sn(C_6H_5)_4$ catalyst in the form given by equation 6 from which the slope, r_1, was found to be 16 and the intercept, r_2, ~ 0.1. Of these two reactivity ratios, r_1 is the more accurate. A precise value for r_2 would require copolymerizations with monomer mixtures containing more propylene than those used here.

TABLE I

INITIAL COPOLYMER COMPOSITION AS A FUNCTION OF MONOMER COMPOSITION FOR THE $AlBr_3-VX_n-Sn-(C_6H_5)_4$ CATALYST

Feed gas composition				Monomer in solution			Initial copolymer			
V.P.C. mole %[a]		Mole fraction		Mole fraction		Weight %	Mole fraction			
Ethylene	Propylene	Ethylene	Propylene	Ethylene	Propylene	Propylene	Ethylene	Propylene	f	F
92.5	4.91	0.95	0.050	0.907	0.093	0.9	0.994	0.0062	160	9.8
90.0	6.05	.936	.064	.888	.112	1.15	.992	.0077	129	7.9
91.0	6.31	.934	.066	.880	.120	1.2	.992	.0081	122	7.3
80.5	15.7	.838	.163	.721	.278	3.5	.977	.0235	41	2.59
70.8	23.7	.750	.252	.620	.380	4.6	.968	.0322	30	1.63

[a] The cylinder also contained 3–5% methane and ethane which are inert in the polymerization and are ignored in the calculations based on monomer mole fractions.

Earlier qualitative experiments carried out at atmospheric pressure indicated a somewhat lower value for r_1 under those conditions. The use of a pressurized reactor and a high-speed agitator was designed to insure that monomer dispersion is not the rate controlling step. In this equipment polymerization can proceed at an instantaneous rate of ≃100 grams of monomer/minute for short periods (until the heat of reaction is excessive).
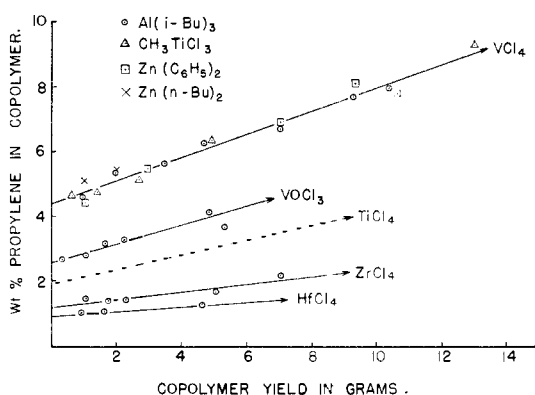

Fig. 5.—Effect of catalyst structure on copolymer composition; monomer contained 23.7 mole % propylene and 76.3 mole % ethylene.

Figure 5 gives representative results obtained when a constant ethylene–propylene mixture was copolymerized with a variety of other organometallic mixed catalysts.[4] The top curve shows that copolymers of the same composition are produced when different reducing agents are used as cocatalysts with a common transition metal compound; however, the use of different transition metal compounds with a common reducing agent, $Al(i\text{-}Bu)_3$, gave copolymers of different composition in every case.

There is abundant evidence from the work of Natta and co-workers that the Ziegler-type catalysts give essentially "ideal" copolymerization[9,10] which is defined as the case where $r_1r_2 \sim 1$. When $r_1r_2 = 1$ equation 5 can be simplified to

$$\frac{dM_1}{dM_2} = r_1 \frac{M_1}{M_2} \qquad (7)$$

which allows one to estimate r_1 from the copolymer composition represented by the intercepts of the curves on Fig. 5, then $r_2 \simeq 1/r_1$. A measure of the validity of this assumption is the fact that the

slopes of the lines, for a given intercept, are the same as for the $AlBr_3-VCl_4-Sn(C_6H_5)_4$ catalyst which was shown to approximate the ideal case.

Natta, Mazzanti, and co-workers[11–15] also have observed differences in comonomer reactivity ratios using catalysts composed of aluminum trihexyl and different transition metal halides, but they did not vary the reducing agent. A comparison of reactivity ratios (Table II) indicates that the

TABLE II

REACTIVITY RATIOS FOR ETHYLENE–PROPYLENE COPOLYMERIZATION WITH ORGANOMETALLIC MIXED CATALYSTS

Catalyst	r_1	Catalyst[a]	r_1
$AlBr_3 + VX_n + Sn(C_6H_5)_4$	16		
$Al(i\text{-}Bu)_3 + VCl_4$	16	$Al(n\text{-}C_6H_{13})_3 + VCl_4$	7.1
$Al(i\text{-}Bu)_3 + VOCl_3$	28	$Al(n\text{-}C_6H_{13})_3 + VOCl_3$	18
$Al(i\text{-}Bu)_3 + TiCl_4$	37	$Al(n\text{-}C_6H_{13})_3 + TiCl_4$	33
$Al(i\text{-}Bu)_3 + ZrCl_4$	61		
$Al(i\text{-}Bu)_3 + HfCl_4$	76		

[a] Taken from the data of ref. 9.

propylene relative reactivity in their case is higher than the values reported here for the three transition metal compounds common to both studies ($TiCl_4$, $VOCl_3$, VCl_4). No specific significance is attached to the fact that the two sets of data are not identical since the experiments were carried out with different reaction diluents, pressures, temperatures, degree of monomer dispersion, and possibly different degrees of reduction of the transition metal. It is significant that the trend is the same in both sets of data.

In the polymerizations described here the transition metal compound was added to a large excess of the reducing agent to insure rapid, maximum reduction in an attempt to reach a common, low transition metal valence. Previously reported valence measurements on several of these catalysts showed that reduction to the divalent state usually occurred under the conditions used here.[3] Natta and co-workers have shown that varying the Al/Ti ratio in the AlR_3-TiCl_4 catalyst caused the relative reactivity of propylene vs. ethylene to decrease with increasing Al/Ti ratio (increasing degree of Ti reduction).[15] In the present case the relative reactivity of propylene vs. ethylene was also higher at low Al/V ratios (0.3~1)(compare Fig. 5 with Fig. 6), and under these conditions the vanadium

(9) (a) G. Natta, J. Polymer Sci., 34, 21, 88 (1959): (b) G. Natta, Manuscript of a Paper Presented at 15th Annual Technical Conference of Society of Plastics Engineers, New York, New York, January 27–30, 1959.'

(10) G. Natta, F. Danusso and D. Sianesi, Makromol. Chem., 30, 238 (1959).

(11) G. Natta, G. Mazzanti, A. Valvassori and G. Pajaro, Chim. e ind. (Milan), 39, 733 (1957).
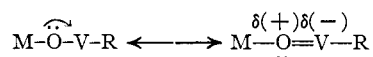
(12) G. Mazzanti, A. Valvassori and G. Pajaro, ibid., 39, 743 (1957).

(13) G. Mazzanti, A. Valvassori and G. Pajaro, ibid., 39, 825 (1957).

(14) G. Natta, G. Mazzanti, A. Valvassori and G. Sartori. ibid., 40, 717 (1958).

(15) G. Natta, A. Valvassori, G. Mazzanti and G. Sartori, ibid., 40, 896 (1958).

is only partially reduced.[3] The scatter in the data is undoubtedly due to the existence of more than one active site and the impossibility of achieving a stable system while chemical change in the catalyst is still occurring. On Fig. 5 experimental points are not given for the TiCl₄ catalyst since more than one active site is known to be present and reproducibility is poor. The copolymer composition distributions reported by Natta and co-workers[11-15] are broader than one would predict from simple statistics[16] and is further support for the presence of more than one catalyst species.

Discussion

Selection between two monomers at the growing polymer chain end is a sensitive measure of the structure and polarity of the active propagation site, and a change in this selectivity implies a change in the nature of the active site. The fact that the relative monomer reactivities are altered by changes in the transition metal center but not by changes in the reducing agent implies that propagation is occurring at the transition metal center.[4] The organotransition metal compound may or may not be complexed with a molecule of another metal compound, but no specific catalytic effect is attributed to the existence of bimetallic complexes.[3,17-19] The reducing agents used here differ widely in general steric configuration and in bond hybridization, electronegativity, valence and size of the metal ion, which should effect at least some change in the monomer selectivity of the growing chain end if these compounds participate in the propagation reaction.

In previous discussions propagation has been envisioned as occurring by π-bonding of the monomer to a low valence transition metal compound followed by a rearrangement step.[3,17-19]

$$\underset{\text{R}'}{\overset{\delta(+)\ \delta(-)}{\text{M---R}}} + CH_2{=}CH_2 \longrightarrow \underset{\underset{\underset{\text{R}'}{\overset{\delta(-)\delta(+)}{\text{R}'}}}{\overset{\text{CH}_2{=}\text{CH}}{\uparrow}}}{\overset{\delta(+)\delta(-)}{\text{M---R}}} \longrightarrow$$

$$\underset{\text{R}'}{\overset{\delta(+)\delta(-)}{\text{M---CH}_2\text{---CH---R}}}$$

Because of the low electronegativity of the transition metal center, M–R bonds will be very polar with carbon carrying a $\delta(-)$ charge relative to the metal. Since the complexed olefin is under the influence of the polar M–R bond, it will in turn be polarized in such a way as to assist migration of the –R group, probably as an anion. The overall reaction is energetically favored to the extent of the heat of saturation of the double bond.

The formation of π-complexes between olefins and platinous, palladous or silver ion[20] is rapidly

(16) W. H. Stockmayer, *J. Chem. Phys.*, **13**, 199 (1945).

(17) (a) W. L. Carrick, *J. Am. Chem. Soc.*, **80**, 6456 (1958); (b) D. B. Ludlum, A. W. Anderson and C. E. Ashby, *ibid.*, **80**, 1380 (1958).

(18) (a) W. L. Carrick, W. T. Reichle, F. Pennella and J. J. Smith, *ibid.*, **82**, 3887 (1960); (b) G. W. Phillips and W. L. Carrick, *J. Polymer Sci.*, in press.

(19) G. L. Karapinka, J. J. Smith and W. L. Carrick, *ibid.*, in press.

(20) (a) S. Winstein and H. J. Lucas, *J. Am. Chem. Soc.*, **60**, 836 (1938); (b) J. S. Anderson, *J. Chem. Soc.*, 1042 (1936).

Fig. 6.—Effect of Al/V ratio on copolymer produced by Al(i-Bu)₃-VCl₄ catalyst; monomer contained 23.7 mole % propylene and 76.3 mole % ethylene. ◯, Al/V ratio = 0.3-1; – – –, Al/V ratio > 10, which also corresponds to the top curve on Fig. 5.

reversible, and by analogy it is also reasonable that the olefin coordination step be reversible in the present case. The migration step is probably effectively irreversible because of the large energy release when the reaction proceeds in the forward direction.

In the above mechanism the rates of both the olefin complexation and rearrangement steps would be altered by a change in the electronegativity (polarity) of the metal center, which predicts that selection between two monomers at the growing chain end would be different for centers of different electronegativity. The observed propylene relative reactivity increased with the series of cocatalysts HfCl₄ < ZrCl₄ < TiCl₄ < VOCl₃ < VCl₄, and the periodic variation in the electronegativity of the metal center follows the same trend (assuming a constant valence).[21] The fact that propylene is less reactive than ethylene with all the catalysts examined likely represents a steric effect; however, increasing propylene reactivity with increasing electronegativity probably represents an electrical effect.

There is also an increase in the electronegativity of the metal center with an increase in valence,[3] and the data of Fig. 6 and ref. 15 show that the relative reactivity of propylene is higher when the transition metal is only partially reduced (but the over-all rate of polymerization and polymer yield is lower in the VCl₄ case). The physical form of the transition metal precipitate is different at different degrees of reduction, so it is difficult to know if the change in relative reactivity is due to the difference in physical form, or to valence, or to both. Previous studies on model organovanadium and organotitanium compounds failed to show catalytic activity at valences >3[18,19]; therefore, it seems unlikely that compounds with valences higher than this are directly contributing to the catalytic function. Epytactic adsorption of the same chemical species (active site) on solids of different electronegativity (valence) could reasonably be expected to change the polarity of the active site sufficiently to account for the above results.

The fact that the active sites are qualitatively different for VCl₄ and VOCl₃ cocatalysts, even

(21) L. Pauling, "Nature of the Chemical Bond," Cornell University Press, Ithaca, New York, 1960. pp. 93–94.

though both are reduced completely to the divalent state under these conditions,[3] is probably due to the presence of the oxygen ligand in the latter case. Resonance forms such as

$$\overset{\frown}{M\text{-}\overset{..}{O}\text{-}V\text{-}R} \longleftrightarrow \overset{\delta(+)\delta(-)}{M\text{---}\overset{..}{O}\text{=}V\text{---}R}$$

would effectively decrease the electron attracting power of the vanadium center and the observed lower relative reactivity of propylene with this system (vs. VCl_4) is in accord with the preceding analysis.

The Crystal Structure of meso-1,4-Diaziridinyl-2,3-butanediol[1]

BY EDWIN S. GOULD AND R. A. PASTERNAK

The crystal structure of the cancer chemotherapeutic agent, meso-1,4-diaziridinyl-2,3-butanediol

$$\begin{array}{ccccc} H_3C & & HO & & CH_2 \\ \diagdown & & | & & \diagup \\ & N\text{---}CH_2\text{---}CH\text{---}CH\text{---}CH_2\text{---}N & \\ \diagup & & | & & \diagdown \\ H_2C & & OH & & CH_2 \end{array}$$
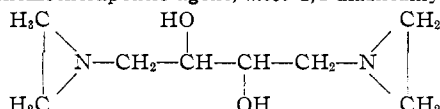
has been determined. The space group is $P2_1/c\text{-}C_{2h}^5$ with two molecules in the unit cell. The diol molecules form a layer-structure perpendicular to the b-plane with hydrogen bonds connecting each –OH group in one layer to a nitrogen atom of an adjacent layer. In common with other structures having three-membered rings, the observed C–C bond length (1.46 Å.) is considerably less than the usual C–C bond length.

The compound 1,4-diaziridinyl-2,3-butanediol,[2]

$$\begin{array}{ccccc} H_2C & & HO & & CH_2 \\ \diagdown & & | & & \diagup \\ & N\text{---}CH_2\text{---}CH\text{---}CH\text{---}CH_2\text{---}N & & (I) \\ \diagup & & | & & \diagdown \\ H_2C & & OH & & CH_2 \end{array}$$
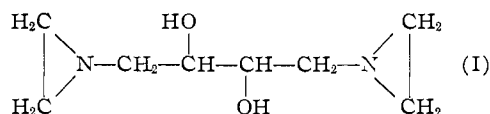
(I) besides exhibiting marked anti-tumor activity, has several features which might warrant structural study. First, no compound having the ethylene-imine (aziridine) ring system appears to have been studied in the solid state,[3] and it seemed likely that the C–C and C–N bond lengths and the exocyclic bond angles associated with this highly strained ring might be significantly different from the usual values existing in unstrained compounds. The nature of the hydrogen bonding in this diol was also of interest, for two modes of intramolecular hydrogen bonding and two more modes of inter-molecular hydrogen bonding were possible. Finally, the compound has been assumed,[2] from the manner of its formation from meso-1,2,3,4-diepoxybutane, to be the meso, rather than the d,l form of the diol, but confirmation of this assignment was desirable.

Experimental

The diol (Fwt. 172.2) crystallizes from ethylene glycol monomethyl ether in platelets. Weissenberg photographs, using Cu $K\alpha$ radiation, established the monoclinic cell dimensions (Å.)

$a = 8.71\ b = 6.98\ c = 7.59$ (each $\pm$ 0.01Å) $\beta = 95.4°$
$V = 460$ Å.[3]

The observed density (obtained by flotation) was 1.25 g./cc., corresponding to 1.99 molecules per unit cell. The plane of the plates corresponds to the bc plane of the cell.

The systematic absences were: $h0l$ if l is odd, and $0k0$ if k is odd. These establish the centrosymmetric space group $P2_1/c\text{-}C_{2h}^5$. The molecule must have a center of symmetry, and the asymmetric unit contains four carbons, a nitrogen, an oxygen and eight hydrogen atoms. The observed space group is consistent with the meso form of the diol but not with the d,l-form.

Zero and upper layer data were taken with multiple films for rotation about the three major axes. For rotation about a, 8 layers were taken; for rotation about b, 6 layers; and for rotation about c, 7 layers. In effect, data were taken in triplicate except for a small number of reflections having high values of sin θ. Intensities were measured by visual comparison with intensity strips. Separate intensity strips were used for each rotation axis since a different crystal was used for each axis. Lorentz and polarization corrections were made in the usual way, and the corrected intensities were normalized to a single scale by cross correlation between the various sets of films. Absorption corrections were not made. For the most part, intensities obtained from rotation about b were given preference in the determination of the structure, but with reflections having k values of 6, 7 or 8, intensities obtained from rotation about the a and/or c axes were used.

Determination of the Structure

Reflections for which $(k + l)$ is even were found to be much stronger than those for which $(k + l)$ is odd, thus indicating that the structure approaches an "a-face-centered" one. Moreover, relative intensities of the corresponding reflections on the $h0l$, $h2l$ and $h4l$ photographs were very similar; the same was true of the corresponding reflections on the $h1l$, $h3l$ and $h5l$ photographs. This distribution indicates a layer-structure with the layers perpendicular to y, separated by the distance $b/2$. In accordance with this picture, the 020 reflection is much more intense than any of the others. Sixty-one intensities were available for the $h0l$ projection. The sharpened Patterson projection[4] along y was calculated. This showed three well-resolved peaks close to the origin. These peaks were used for application of the superposition

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(2) This diol was first prepared by L. Vargha, L. Toldy and E. Kasztreiner, Acta Chim. Acad. Sci. Hung., 19, 295 (1959). It is described in greater detail by E. J. Reist, I. Junga, M. E. Wain, O. P. Crews, L. Goodman and B. R. Baker, J. Org. Chem., in press (1961).

(3) However, microwave studies of gaseous ethyleneimine have been reported by T. E. Turner, V. C. Fiora and W. M. Kendrick, J. Chem. Phys., 23, 1966 (1955).

(4) A. L. Patterson, Z. Krist., 90, 517 (1935).