COMMUNICATIONS TO THE EDITOR

3-DEOXYHEXOSONES

Sir:

The 3-deoxyhexosones are accepted as intermediates in the conversion of sugars by alkali to metasaccharinic acids,[1] and also have been postulated as intermediates in the acid catalyzed production of furfurals from sugars.[2] Yet only the first member of the series, 2-oxopropanal, was known. The two possible 3-deoxy-D-hexosones now have been prepared and their behavior studied under alkaline and acid conditions.

Di-D-fructose-glycine[3] dihydrate[4] (Ia) was heated at 100° for 4.5 minutes in dilute aqueous solution at *p*H 5. Decationization and concentration yielded 3-deoxy-D-*erythro*hexosone (IIIa) as a colorless amorphous solid. Traces of impurities (less than 10%), which included glucose (1–2%) and mannose (1–2%) were removed by chromatography on a paper column giving the pure osone [Found: C, 44.53; H, 6.59]. Di-D-tagatose-glycine[4] (Ib) similarly gave 3-deoxy-D-*threo*hexosone (IIIb). Both osones readily gave osazones (Table I) in the absence of acid.

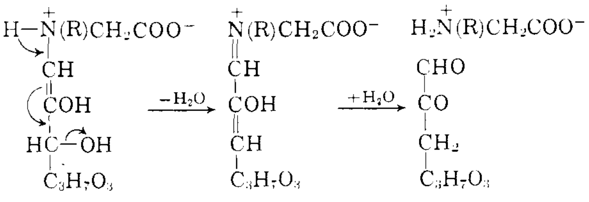
Table I

Substituted Phenylosazones of 3-Deoxyhexosones[a]

Osone	Substituent	M.p., °C. (dec.)	$[\alpha]^{25}\mathrm{D}$
D-*erythro*-	2,4-Dinitro-[b]	266	+800°[c]
	Triacetate	184	+588°[d]
	2,5-Dichloro-	242	+400°[e]
	Triacetate	184	.....
	4-Nitro-[b]	260–262	+350°[c]
D-*threo*	2,4-Dinitro-	258–259	−500°[c]
	Tri-acetate	209	.....
	2,5-Dichloro	225	−208°[e]

[a] All were crystalline and gave satisfactory analyses. [b] Identical with the corresponding osazone from 3-deoxy-D-glucose.[5] [c] Pyridine–acetic acid 1:1. [d] Chloroform. [e] Pyridine.

The formation of a 3-deoxyosone and the Lobry de Bruyn–Alberda van Ekenstein transformation are considered to proceed through a common intermediate, the 1,2-enediol of the sugar.[1] Dehydration of the sugar 1,2-enediol to the 3-deoxyosone is normally a side reaction,[1] but in the case of the diketose-amines the position is reversed and only traces of the epimeric aldoses are formed



I (Enol form) II III

Acids quantitatively converted 3-deoxyhexosones to 5-(hydroxymethyl)-2-furaldehyde ($\lambda_{\max}$ 284 mμ), 2,4-dinitrophenylhydrazone, m.p. 203°. The yields after heating for 2 hours at 100° in 2 *N* acetic acid were 45, 80, and 0.5% from IIIa, IIIb, and fructose, respectively. Alkali converted the 3-deoxyhexosones by an internal reaction of the Cannizzaro type to a mixture of the corresponding metasaccharinic acids. Paper chromatography of the lactones showed only "α-" and "β"-metasaccharinic lactones. The yield of glucometasaccharinic acids[6] from IIIa was 25% after only 5 minutes of standing at 25° in oxygen-free 0.038 *N* lime water. The "β" isomer was isolated as its calcium salt $[\alpha]^{25}\mathrm{D}$ + 22° (*cf.* Nef[7]).

Because the 3-deoxyhexosones are converted rapidly by weak acid and alkali to 5-(hydroxymethyl)-2-furaldehyde and metasaccharinic acids, respectively, and because they give intense browning with amino acids,[3] these highly reactive substances may be significant intermediates in various types of sugar degradations.

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(1) J. C. Speck, Jr., *Advances in Carbohydrate Chem.*, **13,** 63 (1958).

(2) M. L. Wolfrom, R. D. Schuetz and L. F. Cavalieri, This Journal, **70**, 514 (1948).

(3) 1,1′-(Carboxymethylimino)-bis-[1-deoxy-D-fructose].

(4) E. F. L. J. Anet, *Aust. J. Chem.*, **12**, 280 (1959).

(5) E. F. L. J. Anet, unpublished results.

(6) W. M. Corbett and I. Kenner, *J. Chem. Soc.*, 1431 (1955).

(7) J. U. Nef, *Ann. Chem. Liebigs*, **376**, 1 (1910).

(8) E. F. L. J. Anet, *Aust. J. Chem.*, **12**, 491 (1959).

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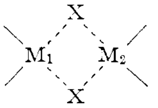
TRANSITION METAL CATALYSTS. III. NATURE OF THE ACTIVE SITE IN ORGANOMETALLIC CATALYSTS

Sir:

There is considerable interest in defining the active species in olefin polymerization catalysts formed from an organometallic reducing agent and a transition metal compound. Since two different compounds are employed and the compounds are usually electron deficient molecules, earlier investigators postulated, and later isolated, bimolecular coördination complexes having the halogen bridge structure[1,2,3]



M_1 = Electropositive metal from organometallic reducing agent such as aluminum.

M_2 = Transition metal of Groups IV-VI of the Periodic Chart (Ti, V, Cr).

Regardless of whether such complexes are essential or not, there is the separate problem of which metal is the site of chain propagation. Our copolymerization studies are pertinent to this problem.

Ethylene and propylene were copolymerized in cyclohexane using a 2-l., vigorously stirred autoclave[4] at 30 p.s.i. and 70°. Catalyst was injected

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(1) G. Natta, P. Pino, G. Mazzanti, E. Mantica and M. Peraldo, *J. Polymer Sci.*, **26**, 120 (1957).

(2) G. Natta, P. Corradini and I. W. Bassi, This Journal, **80,** 755 (1958).

(3) W. L. Carrick, *ibid.*, **80**, 6455 (1958).

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

into the pressurized reactor by hypodermic syringes and the pressure was maintained at 30 p.s.i. with no monomer vented. Copolymer propylene contents were measured by infrared absorption at 7.25 *u*.

Propylene is less reactive than ethylene with all the catalysts employed and it accumulates in the reactor causing a linear increase in the average propylene content of the gross copolymer with increasing yield of copolymer (Fig. 1). Ethylene and propylene show distinctly different relative reactivities with catalysts prepared from a common reducing agent, $Al(i\text{-}Bu)_3$, and different transition metal compounds. Propylene relative reactivity increases in the series $HfCl_4 < ZrCl_4 < TiCl_4 < VOCl_3 < VCl_4$. This increase appears to correspond to increasing electronegativity of the transition metal center. However, there is no significant difference in the relative reactivity of the two monomers when the reducing agent is changed from $Al(i\text{-}Bu)_3$, to $Zn(C_6H_5)_2$, $Zn(n\text{-}Bu)_2$, or CH_3TiCl_3,[6] using a common transition metal compound, VCl_4. These reducing agents differ widely in general steric configuration and in bond hybridization, electronegativity, valence, and size of the metal ion. The common denominator in this series is the reduction of VCl_4 wholly, or partially, to the divalent state.[3,5] Significantly, the two transition metal compounds (CH_3TiCl_3 + VCl_4), form a highly active catalyst and the dependence of copolymer composition on polymer yield is that for VCl_4 catalysts rather than for the $Al(i\text{-}Bu)_3$–$TiCl_4$ catalyst.[7]

Selection between two monomers at the growing 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 occurs at the transition metal center, with no direct participation by the reducing agent.[3] This further suggests that the formation of bimetallic complexes involving the metal of the reducing agent is not an essential feature of the catalytic function.

Natta and co-workers also have observed differences in comonomer reactivity ratios using catalysts composed of aluminum trihexyl and certain transition metal halides,[8] but they did not vary the reducing agent. The available data do not allow a rigorous comparison of the present data with the published results; however, a qualitative comparison indicates that the propylene content of the initial copolymer 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) by a factor of 0.1–0.5. 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 cases. The published opinion of Natta and co-workers[1,8] favors propagation from an aluminum center in a bimetallic complex, although their copolymerization data are more consistent with our view above[3].

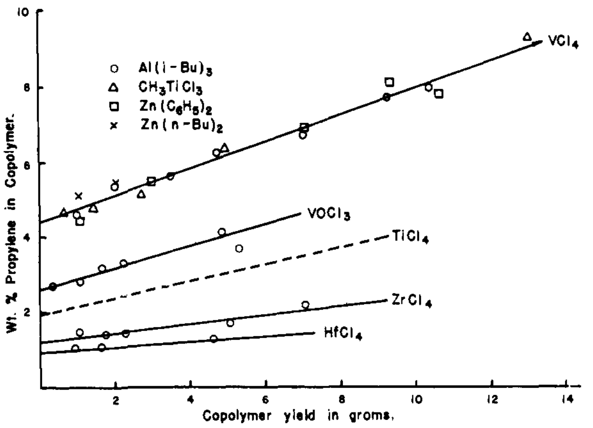

Fig. 1.—Effect of catalyst structure on copolymer composition: in all experiments the monomer feed contained 28% propylene, 69% ethylene and ≃ 3% ethane (area per cent. by vapor chromatography).

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STRONGLY BASIC SOLUTIONS IN TETRAMETHYLENE SULFONE (SULFOLANE)

Sir:

The small autoprotolysis constant and moderately good ionizing characteristics of sulfolane suggest it as a solvent in which one could study a very wide range of acidities.[1] Using solutions of phenyltrimethylammonium hydroxide in aqueous sulfolane, we have been able to measure pK_a's of neutral proton acids distinctly weaker than any previously evaluated by the Hammett method.[2] Table I presents these values along with those of other weak acids obtained by similar methods in aqueous hydrazine[3] and aqueous ethylenediamine.[4]

$H_- = 20$, our most basic value of the H_- function[2] (Fig. 1), is about 4 units more basic than any proper H_- previously evaluated.[3,4] The 0.01 M solution of base in sulfolane containing 5 mole % water is over 10^6 times more basic than the corresponding aqueous solution, *i.e.*, H^- is over 6 units greater. The contribution to this exalted basicity resulting from the reduction of water activity

$$HA + OH^- \rightleftarrows A^- + H_2O$$

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(5) W. L. Carrick, A. G. Chasar and J. J. Smith, Paper No. 4, Polymer Division, 134th Meeting of the American Chemical Society, Chicago, Illinois, September 7–12, 1958.

(6) Belgian Patent 553,447.

(7) Experimental points are not given for the AlR_3–$TiCl_4$ case since more than one active species is present and reproducibility is poor.

(8) G. Natta, *J. Polymer Sci.*, **34**, 21–48, 88–92 (1959).

(1) R. L. Burwell, Jr., and C. H. Langford, THIS JOURNAL, **81**, 3799 (1959).

(2) M. A. Paul and F. A. Long, *Chem. Reviews*, **57**, 1 (1957).

(3) N. C. Deno, THIS JOURNAL, **74**, 2039 (1952).

(4) R. Schaal, *J. Chim. Phys.*, **52**, 784, 796 (1955). We believe that certain details of Schaal's procedures subject his values to substantial error.