COMMUNICATIONS TO THE EDITOR

COORDINATED CATIONIC INITIATOR FOR HIGH cis-1,4-POLYBUTADIENE

Sir:

Evidence presented in this communication indicates that in the case of soluble cobalt initiators[1,2] for polymerizing butadiene to a high cis-1,4 configuration the propagation step occurs through an intermediate carbonium ion rather than a cobalt–carbon bond.[3] Carbon-14 methanol and butanol tritiated on the oxygen were used to stop active butadiene polymerizations initiated by $(C_2H_5)_3Al_2Cl_3$-cobalt octoate. As shown by Feldman and Perry[4] carbon-14 would be bonded to the polymer if a carbonium ion were involved in the chain growth process while tritium would be bonded to the polymer if a carbanion were involved. The C^{14} methanol was purchased from New England Nuclear Corporation and two ml. of tritiated butanol was prepared by an exchange reaction with 0.01 ml. of tritiated water. About 0.2 g. of Linde Molecular Sieve 5A then was added to remove most of the water.

In the polymerization experiments 0.005 millimole of cobalt octoate, 0.05 millimole of $(C_2H_5)_3Al_2Cl_3$ and 150 milliliters of benzene were placed in each of two 250-ml. round-bottom flasks. Butadiene gas then was bubbled into each flask at the same rate. A rapid temperature rise resulted from the formation of high cis-1,4-polybutadiene. After 60 seconds at which time the temperature had increased 15°, one polymerization was stopped with 0.1 ml. of tritiated butanol and the second with 0.1 ml. of carbon-14 methanol. Catalyst residues were removed by twice precipitating the soft tacky polymer with methanol and redissolving in benzene. Polymer activities which were measured by liquid scintillation counting of toluene solutions containing PPO (2,5-diphenyloxazole) and POPOP [2,2-p-phenylenebis(5-phenyloxazole)] were

Shortstop	Shortstop activity (millicuries)	Polymer activity (microcuries/g.)
$C_4H_9OH^3$	0.04	0.008
$^{14}CH_3OH$	0.05	0.96

The small tritium activity was about equal to the background count and can be explained easily by residual moisture in the butanol. Carbon-14 activity, however, can only arise from active carbonium ions on the polymer chains. Assuming that all polymer chains were still growing and were terminated by methanol, one calculates a number average molecular weight of 21,000, which is a reasonable figure based on appearance of the polymer.

These results then show that the growing polymer ion is a cation and not an anion. Failure[3] to find carbon-14 in cis-1,4-polybutadiene prepared with $(^{14}C_2H_5)_2AlCl$-cobalt bisacetylacetonate is thus explained since metal–carbon bonds are most probably not involved. The growing carbonium ion may be associated with a complex anion containing the metals.

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(3) G. Natta, L. Porri and A. Carbonaro, Rendiconti, 29, 491 (1960).
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PHASE DEPENDENCE OF CARBON-11 RECOIL PRODUCTS IN ETHANE AND PROPANE; EVIDENCE FOR METHYLENE INSERTION[1]

Sir:

The recoil product spectrum from ethane in the gas and liquid phases and from propane in the gas, liquid and solid phases shows definite phase dependence.[2] The data provide added evidence for the importance of energy redistribution and deexcitation of the "complex"[3] formed. Further, the products suggested to have been formed by methylene-C^{11} insertion reactions show a predictable yield trend on changing phase, lending additional support for the postulated existence of this reactive intermediate.[4a-h]

The $C^{12}(n,2n)C^{11}$ reaction was used to produce the carbon-11 atoms. The $C^{12}(p,pn)C^{11}$ reaction was used for absolute yield determinations in the gas and liquid phases. The experimental irradiation technique for the $C^{12}(n,2n)C^{11}$ reaction was essentially that described by Suryanarayana and Wolf.[5] The radiation dose delivered to the gaseous samples was 1.4 $\times 10^{-3}$ ev./molecule. The absorbed dose in the liquid and solid was higher for the $C^{12}(n,2n)C^{11}$ reaction and a factor of 10 lower for all comparable runs involving the $C^{12}(p,pn)C^{11}$ reaction. Phillips research grade alkanes further purified by multiple crystallization were used in this work. Analysis of the carbon-11 labeled compounds was done by radio-gas chromatography.[6]

The change from gas to liquid phase causes a drop in the sum of ethylene and acetylene yields (Table I) in both ethane (55 to 33%) and propane (43 to 31%). Lang and Voigt[7] also observed a marked decrease in ethylene and acetylene from cyclohexane [$C^{12}(\gamma,n)C^{11}$] as the temperature of the sample being irradiated was decreased from -30 to $-78°$. A further decrease in these yields is observed for solid propane. Insofar as all or part of the acetylene is formed by carbon atom insertion,[2,4h] followed by fragmentation of the energy-rich "complex"[3] (whether this complex be a discrete intermediate such as an insertion product or whether it be in some more loosely bonded initial state) attenuation of this energy by the surroundings should tend to decrease this degradation provided, (1) the energy of the first formed complex is not too high and, (2) the rate of deexcitation and the rate of internal rearrangement of the "complex" is of the same order of magnitude as the fragmentation reaction. A concomitant increase in three carbon compounds for ethane and four carbon compounds

(1) Research performed under the auspices of the U. S. Atomic Energy Commisssion.
(2) Cf. C. MacKay and R. Wolfgang, Radiochimica Acta, 1, 42 (1962). A preprint of this article "Phase Independence of Major Reaction Mechanisms of Recoil Carbon Atoms" was sent to us by the authors. They studied ethylene, ethylene oxide and isobutane.
(3) Cf. J. Yang and A. P. Wolf, J. Am. Chem. Soc., 82, 4488 (1960).
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(5) B. Suryanarayana and A. P. Wolf, J. Phys. Chem., 62, 1369 (1958).
(6) Cf. F. Cacace, Nucleonics, 19, no. 5, 45 (1961), for a review of this technique. Specific techniques used in this work will be found in G. Stöcklin, F. Cacace, and A. P. Wolf, Z. Anal. Chem., in press.
(7) C. E. Lang and A. F. Voigt, J. Phys. Chem., 65, 1542 (1961).