

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 Perry⁴ 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 C¹⁴ 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 ₄ H ₉ OH ³	0.04	0.008
¹⁴ CH ₃ OH	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. Failure³ 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.

UNITED STATES RUBBER COMPANY
RESEARCH CENTER
WAYNE, NEW JERSEY

C. W. CHILDERS

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(1) C. Longiave, R. Castelli and G. F. Croce, *La Chimica E L'Industria*, **43**, 625 (1961).

(2) M. Gippin, *I & EC Prod. Res. and Develop.*, **1**, 32 (1962).

(3) G. Natta, L. Porri and A. Carbonaro, *Rendiconti*, **29**, 491 (1960).

(4) C. F. Feldman and E. Perry, *J. Polymer Sci.*, **46**, 217 (1960).

PHASE DEPENDENCE OF CARBON-11 RECOIL PRODUCTS
IN ETHANE AND PROPANE; EVIDENCE FOR
METHYLENE INSERTION¹

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-C¹¹ insertion reactions show a predictable yield trend on changing phase, lending additional support for the postulated existence of this reactive intermediate.^{4a-b}

The C¹²(n,2n)C¹¹ reaction was used to produce the carbon-11 atoms. The C¹²(p,pn)C¹¹ reaction was used for absolute yield determinations in the gas and liquid phases. The experimental irradiation technique for the C¹²(n,2n)C¹¹ reaction was essentially that described by Suryanarayana and Wolf.⁵ The radiation dose delivered to the gaseous samples was 1.4×10^{-3} ev./molecule. The absorbed dose in the liquid and solid was higher for the C¹²(n,2n)C¹¹ reaction and a factor of 10 lower for all comparable runs involving the C¹²(p,pn)C¹¹ 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 Voigt⁷ also observed a marked decrease in ethylene and acetylene from cyclohexane [C¹²(γ ,n)C¹¹] 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,^{2,4b} 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 Commission.

(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).

(4) (a) A. P. Wolf, B. Gordon and R. C. Anderson, *ibid.*, **78**, 2657 (1956).

(b) A. P. Wolf, C. S. Redvanly and R. C. Anderson, *ibid.*, **79**, 3717 (1957).

(c) C. MacKay and W. F. Libby, *ibid.*, **79**, 6366 (1957). (d) B. Gordon and A. P. Wolf, Brookhaven National Laboratory Annual Report, BNL-523, AS-12, 51, 1958. (e) Cf. reference 5. (f) A. P. Wolf, *Ann. Rev. Nucl. Chem.*, **10**, 259 (1960). (g) A. P. Wolf, "Chemical Effects of Nuclear Transformations," IAEA, Vienna, 1961, Vol. II. (h) C. MacKay, M. Pandow, P. Polak and R. Wolfgang, *ibid.*, reference 4g.

(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).

TABLE I
CARBON-11 CONTAINING PRODUCTS RESULTING FROM THE C¹²(n,2n)C¹¹ REACTION OCCURRING IN ETHANE AND PROPANE

Compound	Ethane ^a		Propane ^a				
	Gas 1 atm. 25°	Liquid -166°	Gas ^b 1 atm. 25°	Gas 0.58% O ₂ 1 atm. 25°	Gas 14.0% O ₂ 1 atm. 25°	Liquid -78°	Solid -166°
Carbon monoxide	0.8 ± 0.1	<0.5	0.4 ± 0.1	15.6	23.8 ± 2.0	0.6 ± 0.1	0.2 ± 0.1
Methane	2.1 ± 0.1	3.7 ± 0.1	2.9 ± 0.3	0.5	<0.5	3.4 ± 0.3	4.7 ± 0.2
Acetylene	31.2 ± 1.8	17.4 ± 0.5	25.0 ± 0.6	26.0	21.5 ± 1.0	18.2 ± 0.2	11.2 ± 0.6
Ethylene	23.7 ± 0.2	15.7 ± 0.1	17.9 ± 0.3	14.2	10.3 ± 0.5	12.8 ± 1.0	8.9 ± 0.6
Ethane	1.1 ± 0.1	0.9 ± 0.1	1.7 ± 0.3	<0.5	<0.5	<0.0	0.4 ± 0.1
Allene	...	2.0 ± 0.1	1.6 ± 0.8	1.5	1.4 ± 0.3	1.6 ± 0.1	0.8 ± 0.1
Propyne	2.9 ± 0.5	3.4 ± 1.3	1.6 ± 0.5
Propene	4.7 ± 0.6	13.3 ± 0.1	12.2 ± 1.8	6.2	4.5 ± 0.5	7.0 ± 0.4	5.1 ± 0.1
Propane	12.6 ± 0.6	11.5 ± 0.3	<1.0	<0.5	<0.5	0.6 ± 0.1	0.5 ± 0.1
1-Butene	} <3.0	2.4	1.8 ± 0.3	8.1 ± 1.2	7.4 ± 0.7
<i>i</i> -Butene		1.8	1.4 ± 0.4	2.4 ± 0.9	} 4.0 ± 0.5
Other butenes	<2.0	
<i>i</i> -Butane	5.7 ± 0.3	1.6	1.1 ± 0.1	3.2 ± 0.1	3.1 ± 0.4
<i>n</i> -Butane	4.4 ± 0.8	4.0	3.1 ± 0.1	9.6 ± 1.1	9.0 ± 0.7
Higher boiling	23.8	35.0	24.2	23.2	26.7	27.6	43.3

^a Percentages represent the total activity in the gas phase; liquid and solid samples were converted to gases after the runs.

$$\frac{\text{gas phase activity}}{\text{total activity produced}} = 0.95$$

$$\frac{\text{liquid phase activity}}{\text{total activity produced}} = 0.9$$

The reproducibility of each result is listed as a standard deviation. ^b The values in this column agree within reasonable limits with those of MacKay, *et al.*^{4b} With 1.6% added oxygen, Wolfgang and MacKay find the yields of *n*-butane and isobutane to be 3.9 and 2.0% respectively. We find 3.2 and 1.7% at this particular concentration.

for butane is found when the phase is changed, accompanied by an increase in higher boiling compounds in each case. An approximate threefold increase in propene from ethane and in the butenes from propane is significant if we consider them to result from stabilization of the first formed carbenes. Deexcitation is facilitated in the liquid and solid phases thereby increasing the probability of formation of C₃, C₄ and higher hydrocarbons in each instance.⁸

The more marked change in ethylene yields with added oxygen *versus* the relative insensitivity of acetylene yields at equivalent oxygen concentrations may be due to the chemical nature and energy states of the intermediates resulting from carbon insertion and methylene insertion. It should be noted here that a distinction is to be made between the thermal radical scavenging activity of oxygen which reaches a peak of effectiveness in the alkanes we have studied at or below 0.5 vol. % (e.g., the near elimination of methane and ethane from propane, the reduction in ethylene yield, the elimination of the radical component in the production of *n*- and isobutane from propane and similarly propane (13 to 3%) from ethane, in the gas phase, *etc.*) and its action as a competitive reactant for the more energetic ("hot") fragments at higher concentration, *i.e.* > 0.5 vol. % O₂.

The ratio of *n*-butane to isobutane and the absolute yields of these compounds in the three phases follow the prediction based on the deexcitation and methylene insertion hypotheses. Our observation on the *statistical nature* of the formation of the various hexanes from pentane in the liquid phase^{4d,f} led us to extend the gas phase study of MacKay, *et al.*,^{4b} on propane, to the liquid and solid phase. As expected, the absolute yield of the assumed methylene insertion products went up (5.4 to 12.8%) and the ratio of the products approached the statistical one (3/1) yielding a compelling parallelism with the work of Doering, *et al.*⁹ The significance of the gas phase ratio^{4b} while in general agreement with the suggestion of methylene insertion bears

(8) Cf. C. MacKay and R. Wolfgang, *J. Am. Chem. Soc.*, **83**, 2399 (1961), discuss the deactivation of the gaseous species. The limited study of the C₃ fraction from isobutane² did not allow extension of this view.

(9) (a) W. von E. Doering, R. G. Buttery, R. G. Laughlin and N. Chandhuri, *J. Am. Chem. Soc.*, **78**, 3224 (1956). Cf. (b) D. Richardson, M. C. Simmons and I. Dvoretzky, *ibid.*, **83**, 1934 (1961).

closer examination since it can be seen that the absolute yield goes down with increased O₂ and the ratio approaches the statistical one. We interpret this to mean that the radical (both free radical and perhaps also triplet methylene¹⁰) component is eliminated and only those butanes formed from energetic or excited methylene are seen as product. It is also interesting to study this ratio in light of the recent work by Frey and Stevens on the insertion ratios as a function of the source of methylene.¹¹

The propane yield from ethane in the gas (O₂ added) and liquid phases has a comparable behavior pattern.

That insertion mechanisms are involved in these reactions seems reasonable. The assumption of collision complex formation and subsequent deexcitation thereof is also consistent with what is known to date. Certainly the classic criteria of "hot" products (insensitivity to scavenger and lack of phase dependence) applies to few, if any, of the products observed here. The nature of the "primary" process or first significant reaction responsible for each product ultimately formed still needs further study particularly in the liquid and solid phases. The evidence presented here is consistent with the hypothesis that the majority of products formed, result from reactions of carbon occurring at or near thermal energies.

(10) Cf. W. von E. Doering and H. Prinzbach, *Tetrahedron*, **6**, 24 (1959).

(11) H. M. Frey and I. D. R. Stevens, *Proc. Chem. Soc.*, 79 (1962). Cf. B. S. Rabinovitch and D. W. Setser, *J. Am. Chem. Soc.*, **83**, 750 (1961).

CHEMISTRY DEPARTMENT
BROOKHAVEN NATIONAL LABORATORY
UPTON, LONG ISLAND, NEW YORK

GERHARD STÖCKLIN
ALFRED P. WOLF

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THE "CROSS-β" STRUCTURE IN POLY-O-ACETYL-L-SERINE

Sir:

A "β" structure for oriented films of poly-O-acetyl-L-serine has been assigned by Fasman and Blout,¹ based on the results of polarized infrared spectroscopy. However, we found two conformations of this polypeptide in films prepared by two different methods. An oriented film obtained by directional rubbing with a spatula of a very viscous solution of polypeptide in tri-

(1) G. D. Fasman and E. R. Blout, *J. Am. Chem. Soc.*, **82**, 2262 (1960).