

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	Liquid	Gas ^b	Gas		Liquid	Solid
	1 atm. 25°	-166°	1 atm. 25°	0.58% O ₂ 1 atm. 25°	14.0% O ₂ 1 atm. 25°	-78°	-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.*^{4h} 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.*,^{4h} 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^{4h} 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).

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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).

fluoroacetic acid was found to have a "cross- β " structure² (see Fig. 1a). Stronger rubbing in one direction produced a film with a "parallel- β " structure (see Fig. 1b).

For the (a) film, the parallel dichroism of the 1632 cm^{-1} (amide I of a " β " conformation) and the 3328 cm^{-1} (NH stretching) bands, and the perpendicular dichroism of the 1514 cm^{-1} (amide II) band indicate that this film exists in a "cross- β " structure.³ Furthermore, the perpendicular dichroism of the 1700 cm^{-1} band indicates antiparallel peptide alignment.^{4,5} In the (b) film, the dichroism is weak compared with the (a) film, but suggests that this conformation corresponds to a "parallel- β " structure.

The molecular weight of this poly-O-acetyl-L-serine (Sample No. 211, which was synthesized by polymerization of O-acetyl-N-carboxy-L-serine anhydride) was estimated from the intrinsic viscosity value ($[\eta] = 0.12_3$) in trifluoroacetic acid, using the empirical equation⁶ of Doty, Bradbury and Holtzer. It was *ca.* 10,000.

In connection with these observations two interesting points can be raised. First, some natural proteins, for example epidermin,⁷ exhibit the "cross- β " to "parallel- β " transformation observed by us on poly-O-acetyl-L-serine. In addition, these proteins are rich in serine. It is supposed then, that the mechanism of "cross- β " and "parallel- β " transition is identical in natural proteins and poly-O-acetyl-L-serine.

Secondly, the synthetic polypeptides which have been reported with a pure "cross- β " structure are only of low degree of polymerization,^{3,5} and in these cases the low molecular weight polypeptide chains seem to be running side by side at right angles to the fiber axis. In a polypeptide of not too low molecular weight, poly- β -benzyl-L-aspartate, the " ω " form and "cross- β " mixture obtained by heating to about 160° has been reported.³ In the case of poly-O-acetyl-L-serine the molecular weight is not so low, while the "cross- β " structure is quite predominant. Therefore, two interpretations can be proposed for the structure of the "cross- β " configuration of poly-O-acetyl-L-serine: namely, the polypeptide chains are fully extended and align at right angles to the fiber axis as reported for low molecular weight "cross- β " structure, or one polypeptide chain is folded transversely like Rudall's model for epidermin.

The former requires interchain hydrogen bonds between peptide groups, while the latter would have intrachain hydrogen bonds. There has been no direct confirmation of either bond type in the structure of poly-O-acetyl-L-serine. However, if the "cross- β " structure observed in the solid state exists in solution where " β " conformation has been assigned from infrared solution spectroscopy,^{1,8} indirect evidence for the existence of the intrachain "cross- β " structure is found by its behavior on dilution. The values of the optical rotation of poly-O-acetyl-L-serine at $\lambda = 546 \text{ m}\mu$ in solutions of dichloroacetic acid or trifluoroacetic acid (10–25%) and chloroform (90–75%) mixtures are little dependent on the polymer concentration⁸ while the $[\alpha]_{546}$ of interchain " β " polypeptide is remarkably dependent on the concentration.^{9,10} These observations on the concentra-

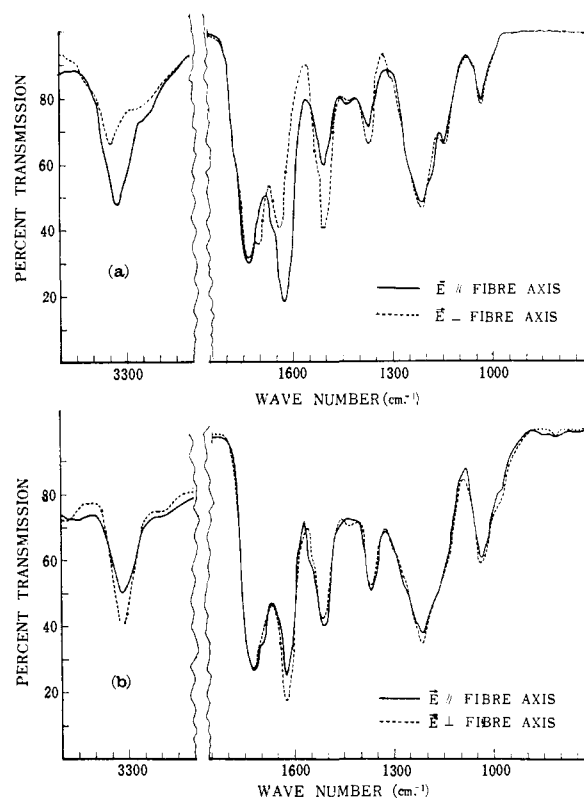


Fig. 1.—Infrared spectra of oriented film of poly-O-acetyl-L-serine: —, electric vibration direction parallel to fiber axis; ---, electric vibration direction perpendicular to fiber axis; (a) shows cross- β structure; (b) shows parallel- β structure.

tion dependence of optical rotation suggest that the intramolecular " β " structure exists in poly-O-acetyl-L-serine solution. As a further evidence, detailed studies on X-ray analysis have been carried out¹¹ though some preliminary X-ray works have been suggested to be done.²

(11) I. Yahara, K. Imahori, Y. Itaka and M. Tsuboi, *J. Polym. Sci.*, in press.

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THE DETERMINATION OF THE STABILITIES OF SCHIFF BASE COMPLEXES INVOLVING DISSOCIATED SCHIFF BASES

Sir:

Increasing interest has lately been focused on the properties of Schiff base complexes especially with regard to their role in non-enzymatic transamination reactions.^{1–7} While the stabilities of the complexes with the more stable Schiff bases can be obtained readily⁸ few studies seem to have been reported concerning those complexes in which the Schiff base itself is appreciably dissociated. The investigations described in refs. 2, 4, 5, and 7 concern such cases. These investigations were carried out spectrophotometrically and because of the difficulties encountered in interpreting the results when spectrally similar species are involved it was necessary either to arrange conditions so only Schiff base complexes having a ratio of metal ion

(2) C. Johnson and C. Cohen "quoted in reference 1" assigned the cross- β structure to poly-O-acetyl-L-serine from X-ray diffraction investigation.

(3) E. M. Bradbury, L. Brown, A. R. Downie, A. Elliott, D. B. Fraser, W. E. Hanby and T. R. R. McDonald, *J. Mol. Biol.*, **2**, 276 (1960).

(4) T. Miyazawa and E. R. Blout, *J. Am. Chem. Soc.*, **83**, 712 (1961).

(5) M. Tsuboi and A. Wade, *J. Mol. Biol.*, **3**, 480 (1961).

(6) P. Doty, J. A. Bradbury and A. M. Holtzer, *J. Am. Chem. Soc.*, **78**, 947 (1956).

(7) K. M. Rudall, *Advances in Protein Chem.*, **7**, 253 (1952).

(8) I. Yahara and K. Imahori, in preparation.

(9) J. T. Yang and P. Doty, *J. Am. Chem. Soc.*, **79**, 761 (1957).

(10) A. Wada, M. Tsuboi and E. Konishi, *J. Phys. Chem.*, **65**, 1119 (1961).

(1) D. E. Metzler and E. E. Snell, *J. Am. Chem. Soc.*, **74**, 979 (1952).

(2) G. L. Eichhorn and J. W. Dawes, *ibid.*, **76**, 5663 (1954).

(3) B. Witkop and T. W. Beiler, *ibid.*, **76**, 5589 (1954).

(4) H. N. Christensen, *ibid.*, **80**, 2305 (1958).

(5) L. Davis, F. Roddy and D. E. Metzler, *ibid.*, **83**, 127 (1961).

(6) H. Mix, *Z. physiol. Chem.*, **315**, 1 (1959).

(7) L. J. Nunez and G. L. Eichhorn, *J. Am. Chem. Soc.*, **84**, 901 (1962).

(8) T. J. Lane and A. J. Kandathil, *ibid.*, **83**, 3782 (1961).