$$(4)$$

Presumably it corresponds to the compound [PtH$_2$Cl$_2$-(PEt$_3$)$_2$], prepared by Chatt and Shaw[2] by passing dry HCl through an ether solution of *trans*-PtHCl(PEt$_3$)$_2$ and reported by them to decompose by loss of HCl to regenerate *trans*-PtHCl(PEt$_3$)$_2$ on heating or on treatment with water. We are presently attempting to prepare the isotopically substituted compound [Pt-HDCl$_2$(PEt$_3$)$_2$] by the corresponding reaction with DCl, to establish its structure, and to examine its decomposition.

No explanation is available for the apparently higher than first-order kinetic dependence of the Cl⁻-dependent exchange path in solvents of low D$_2$O content. A difficulty connected with the interpretation of these results is that ionic dissociation is probably incomplete under these conditions so that the apparent kinetic dependence on the Cl⁻ concentration may include the effects of ionic association equilibria (possibly involving HCl$_2$⁻).

The above interpretation predicts that the Cl⁻-catalyzed exchange between *trans*-PtHCl(PEt$_3$)$_2$ and D$_2$O should be accompanied by exchange of the Cl ligand of the complex with isotopically labeled Cl⁻ in the solution. Experiments with ³⁶Cl⁻ (designed to test this) revealed that, under the conditions of these experiments, chloride exchange occurs much more rapidly than hydrogen exchange, apparently by a direct mechanism which does not involve acid catalysis. This is consistent with earlier observations[3,4] that the chloride ligand of *trans*-PtHCl(PEt$_3$)$_2$ is rapidly substituted by pyridine in ethanol solution. The results of the chloride-exchange experiments are thus consistent with, but provide no supporting evidence for, the mechanism proposed for the hydride exchange.

(3) F. Basolo, J. Chatt, H. B. Gray, R. G. Pearson, and B. L. Shaw, *J. Chem. Soc.*, 2207 (1961).
(4) C. D. Falk and J. Halpern, *J. Am. Chem. Soc.*, 87, 3003 (1965).

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Propagation Mechanism in Strong Base Initiated Polymerization of α-Amino Acid N-Carboxyanhydrides

Sir:

The mechanism in the strong base initiated polymerization of α-amino acid N-carboxyanhydrides (NCA's) has been the subject of much controversy.[1]

(1) C. H. Bamford and H. Block, "Polyamino Acids, Polypeptides

A plausible initial step for N-unsubstituted NCA's involving the removal of the N–H proton by the base to produce an N-carboxyanhydride anion (NCA⁻) was proposed by Bamford[1] and established by Goodman and Arnon.[2]

Two propagating routes have been postulated. Bamford[1] contended that the NCA⁻ ion attacks the carbonyl of an NCA molecule to create a dimer, I, terminated by a carbamate ion. This ion, he suggested, can remove a proton from another monomer molecule, recreating NCA⁻, or it can abstract a proton from the protonated base (in the tertiary amine initiated case). Both possible reactions convert compound I to the corresponding carbamic acid which loses carbon dioxide to produce an amine-terminated dimer, II.

Bamford considered that this amine group could propagate by carbonyl attack on monomer molecules. Such a mechanism could not account for the observed high rate. However, he also proposed a possible propagating step in which the activated monomer (NCA⁻) attacks the NCA terminal group of II, opening the ring and producing compound III. The resulting carbamate ion again reacts with NCA to create NCA⁻ and carbon dioxide. Repetition of these rapid steps produces the polypeptide.

The alternative suggested by Blout[3] would simply have the carbamate ion I act as a nucleophile instead of a base. It attacks the NCA carbonyl to yield a mixed carboxylic-carbamic anhydride IV containing a carbamate ion at the chain end. Elimination of carbon dioxide is proposed to occur rapidly from such a mixed anhydride.

Work carried out by Goodman and Arnon[4] showed that polymerization initiated by sodium N-benzylcarbamate gives identical kinetics with those of a strong base such as sodium methoxide. This appeared to support Blout's carbamate propagation route.
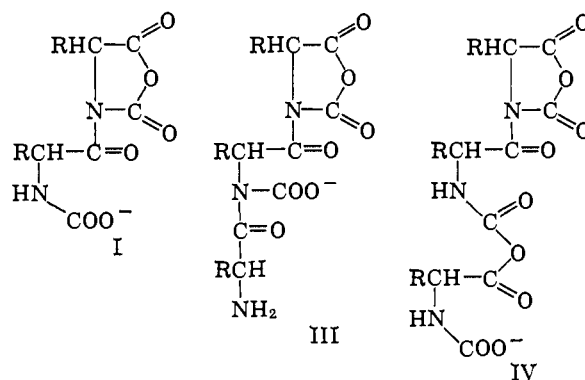
In order to distinguish between the Blout and Bamford proposals we extended the Goodman and Arnon carbamate experiments to include initiation by ¹⁴C-labeled sodium N-benzylcarbamate. Blout's proposal would be established if the polymer contained all the radioactive initiator fragments. Recently, in an excellent review on the subject of NCA polymerization,[5]

and Proteins," M. A. Stahmann, Ed., University of Wisconsin Press, Madison, Wis., 1962, p. 65.
(2) M. Goodman and U. Arnon, *Biopolymers*, 1, 500 (1963).
(3) M. Idelson and E. R. Blout, *J. Am. Chem. Soc.*, 80, 2387 (1958).
(4) M. Goodman and U. Arnon, *ibid.*, 86, 3384 (1964).
(5) M. Szwarc, *Advan. Polymer Sci.*, 4, 1 (1965).

Szwarc suggested essentially the same experiment, in addition to clarifying the Bamford mechanism.

Radioactive (^{14}C) benzylamine (3 g., 0.5 mcurie, supplied by Nuclear Research Chemicals, Inc.) was converted to the sodium N-benzylcarbamate using carbon dioxide and a sodium methoxide–methanol solution as described previously.[4] The carbamate was dissolved in anhydrous methanol and standardized by titrating the carbon dioxide evolved upon addition of sulfuric acid.

The preparation and purification of γ-benzyl-L-glutamate NCA and method of polymerization, measurement of kinetics, determination of molecular weight, and radioactive counting have also been discussed previously.[4]

Polymerizations of γ-benzyl-L-glutamate NCA with both radioactive and nonradioactive carbamate in tetrahydrafuran solutions showed the same results. The rates were high, giving an average k_p at 25° of about 3.0 l./mole sec. This value is close to that observed with sodium methoxide initiation. Of prime importance, however, is the fact that only 2.5–3.0% of the radioactivity was found in the isolated polymer. Thus, we conclude that the mixed anhydride mechanism cannot be valid. The Bamford–Szwarc mechanism has not been positively proven but it is now clearly the best possibility.

Additional support for this interpretation comes from the observation of a large induction period and a degree of polymerization significantly higher than the anhydride/initiator ratio (A/I). If nucleophilic carbamate ion were the propagating species no induction period would be observed because the initiation step would be by-passed. Also, since each molecule of carbamate would produce one growing chain, the A/I would be nearly equal to the degree of polymerization.

The carbamate ion can remove weakly acidic protons in spite of its weak basicity because subsequent decarboxylation of the resulting carbamic acid continuously shifts the following equilibrium to the right:
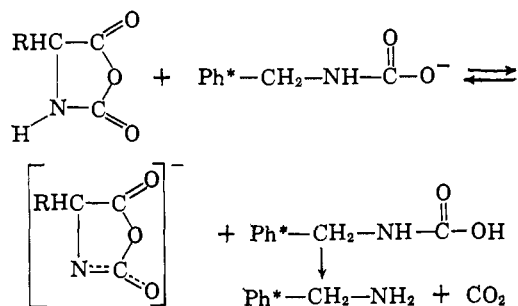
We can explain the appearance of the small amount of radioactivity in the polymer from initiation by radioactive benzylamine, produced as above. Such a polymerization would follow slow kinetics, leading to the incorporation of only a small amount of activity in the polymer.

A very good analogy can be drawn between this activated monomer propagation mechanism and that of the anionic polymerization of caprolactam as presented by Wichterle.[6]

Work in progress on N-substituted NCA's indicates that a different polymerization mechanism is operative.

(6) O. Wichterle, J. Sebenda, and J. Kralicek, Advan. Polymer Sci., 2, 578 (1961).

A complete report of our findings, in which we will include our investigations on radioactive primary, secondary, and tertiary amine initiators, will appear shortly.

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Electrochemical Syntheses. V. The Synthesis of Methyl Esters of α,β-Unsaturated Carboxylic Acids from Olefins and Carbon Monoxide

Sir:

Although various reactions of olefins with carbon monoxide have been reported,[1-3] the synthesis of α,β-unsaturated carboxylic acids or esters from olefins and carbon monoxide has been unsuccessful as yet.

We wish to report here the first direct synthesis of methyl esters of α,β-unsaturated carboxylic acids from olefins and carbon monoxide by a unique electrochemical method in the presence of a platinum-carbonyl complex

$$C_6H_5CR{=}CH_2 + CO + CH_3O^- \xrightarrow[{[Pt_2(CO)_y]^n}]{\text{anode}} C_6H_5CR{=}CHCOOCH_3$$

$$R = H, CH_3, C_6H_5$$
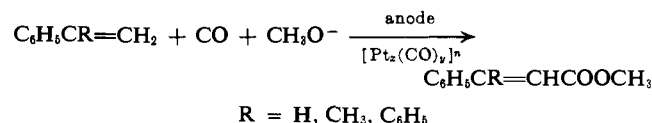
The electrolysis was carried out by using a platinum plate (2 × 3 cm.^{2}) as the anode in a cylindrical glass cell placed in an autoclave (500 cc.) under a pressure of 70 kg./cm.^{2} of carbon monoxide in the following way. First, by using a platinum plate (2 × 3 cm.^{2}) as the cathode, the platinum carbonyl complex[4] was produced in methanol solution containing sodium methoxide (metallic sodium, 0.5 g., in 90 g. of methanol) by electrolysis for 5–10 hr. Then, by using a copper plate (2 × 3 cm.^{2}) as the cathode, the electrolysis was carried out in the presence of olefins and carbon monoxide for 16 hr. The current was controlled at approximately 1.0 amp. and the temperature was kept at −10 to −15°.

The electrolysis of styrene (15.6 g., 0.15 mole) in the presence of platinum-carbonyl complex (1.5 g. of Pt) under these conditions gave methyl trans-cinnamate (I), m.p. 35–36° (5.0 g., 21%), which was contaminated with methyl β-methoxy-β-phenylpropionate (II, 3.9 g., 13%), methyl β-phenylpropionate (III, 0.4 g., 1%), and styrene glycol dimethyl ether (IV, 5.7 g., 23%).

(1) M. Orchin and I. Wender, Catalysis, 5, 6 (1957).
(2) C. W. Bird, Chem. Rev., 62, 283 (1962); W. Reppe, Ann., 582, 38 (1953).
(3) M. A. Bennett, Chem. Rev., 62, 611 (1962).
(4) When the electrolysis of methanol containing sodium methoxide (metallic sodium, 0.5 g., in 90 g. of methanol) was carried out by using two platinum plate electrodes (2 × 3 cm.^{2}) in the presence of carbon monoxide (70 kg./cm.^{2}) for 5–10 hr (1.0 amp., 16–45 v.), the platinum plate used as the cathode was easily dissolved into the solution to give a platinum–carbonyl complex, which was isolated by the removal of methanol from the electrolyzed solution under dry nitrogen atmosphere. This carbonyl complex is very air sensitive and greenish blue.