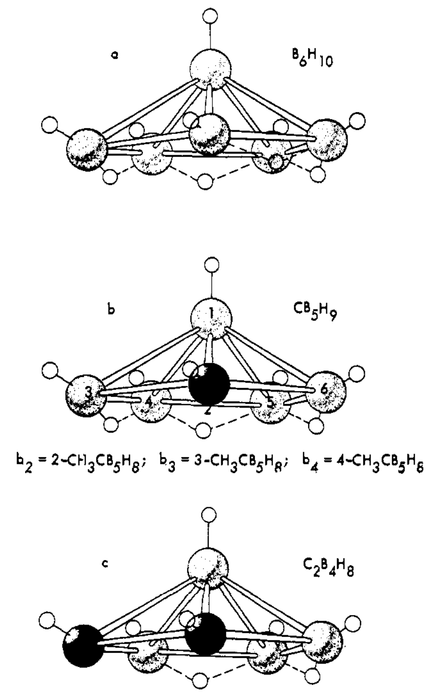

Figure 3. The structure of 2-carbahexaborane(9) and related species.

B–H components, a strong signal assigned to the CH_3 group at τ 8.3, 9.5, and 9.9 ppm for the 2-, 3-, and 4-methyl compounds, respectively. A less intense peak at τ 4.5 in the 3- and 4-methyl isomers represents the skeletal C–H group which is absent in the 2 isomer. This not only supports the proposed structure, but also eliminates an alternative structure for b_2 in Figure 3 which has a hydrogen atom as well as a CH_3 group on the skeletal carbon atom and one less bridge hydrogen atom.

A number of possible mechanisms should be considered to account for the formation of these compounds and the consequent proton and methyl group migrations. The constitution of the products suggests the initial formation of a vinylpentaborane intermediate followed by intramolecular hydroboration and rearrangement. Chemical and isotopic tracer experiments are presently underway to test this scheme as well as to reveal whether or not the 2-methyl isomer is the initial product which rearranges to the others (the 3-methyl isomer is the most abundant).

These derivatives of CB_5H_9 represent a new series of carboranes of the general formula CB_nH_{n+4} (one carbon atom, three bridge hydrogens) which may be added to the other classes of carboranes, *i.e.*, $C_2B_nH_{n+2}$ (two carbon atoms, no bridge hydrogens),[2,3] $C_2B_nH_{n+4}$ (two carbon atoms, two bridge hydrogen atoms),[4] and CB_nH_{n+2} (one carbon atom, one bridge hydrogen).[5] In Figure 3, the structural similarity of CB_5H_9 (b) to B_6H_{10} (a)[6] and $C_2B_4H_8$ (c) may be seen. The two carboranes result from the successive substitution of BH_2 groups (one bridge and one terminal hydrogen atom) in B_6H_{10} by isoelectronic CH groups. It is apparent that similar substitution in other borane systems should result in additional series of carborane species.

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Regulation of Rate of Reaction of a Polyuridylic Acid Derivative by Use of Suppressor and Antisuppressor Molecules[1,2]

Sir:

It has been demonstrated that the rate of a reaction involving transformations of functional groups X and Y in RX and R′Y may be unusually high when R and R′ bear ionic charges of opposite sign.[1,3] This phenomenon may be attributed to the molecular organization effected by the attractive forces between R and R′. In the present communication it is shown that the rate of reaction in such systems may be controlled, that is, successively decreased and increased at will, by additions to the reaction medium of substances which are chemically inert in the usual sense yet in extremely low concentrations serve as rate regulators. The principle of controlling reaction rates by means of chemical regulators may prove useful in developing a chemistry of complex molecules which react sequentially in a highly selective manner, such as found in biological systems.

A nitrophenyl ester derivative of polyuridylic acid was selected as RX. In solution at pH 8.5 this polymer is negatively charged, and it possesses ester groups which on reaction with imidazole derivatives afford nitrophenoxide, easily detected by the ultraviolet spectrum. It was prepared by warming polyuridylic acid ammonium salt[4] with excess succinic anhydride and pyridine in formamide for 6 hr at 65°, isolating the succinoylated derivative by chromatography in water on Sephadex G-25 followed by lyophilization, and esterifying the succinate derivative with nitrophenol and dicyclohexylcarbodiimide in formamide and pyridine. The resulting polymer (I), purified by chromatography on Sephadex, contained 0.44 nitrophenyl group per uridine unit as indicated by the ultraviolet spectra before and after alkaline hydrolysis. From the method of preparation and the properties of the substance it is probable that the nitrophenyl succinate

[1] Part V in the series on Selective Catalysis. Part IV: R. L. Letsinger and I. S. Klaus, *J. Am. Chem. Soc.*, **87**, 3380 (1965).

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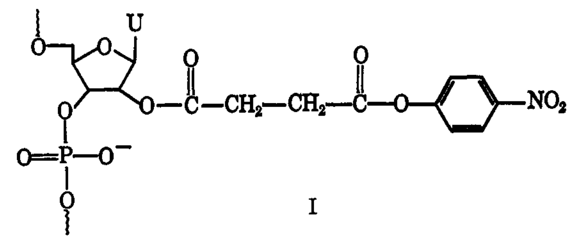
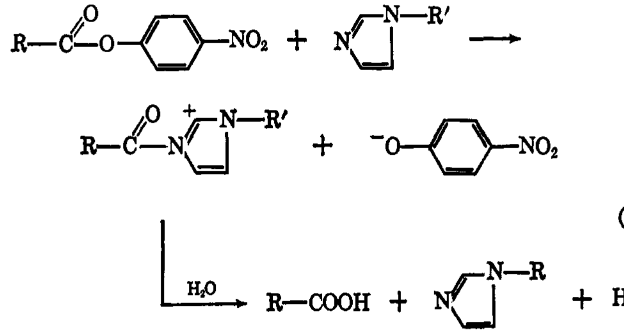


I

moiety is joined primarily at the 2′ position. Poly(N-vinylimidazole)[5] was chosen for the R′Y component. The net reaction with I in water may be represented by eq 1. The experiments were carried out in 3 ml of 0.067 *M* aqueous sodium bicarbonate solution,



(1)

formation of nitrophenol being followed by the increase in absorbance at 400 mμ. Rate data are expressed in Table I as "initial first-order rate constants," $k^{\text{i}}_{\text{obsd}}$.[6] A striking feature of the reactions is that polyvinylimidazole at low concentrations (3.3×10^{-5} *M* in imidazole units) is about 300 times as effective as an equivalent amount of imidazole in liberating nitrophenol from *p*-nitrophenyl poly U succinate (I). It is interesting that poly-L-histidine, which forms a gelatinous precipitate in water at pH 8.5, reacts even more rapidly than poly(N-vinylimidazole) with substrate I. This system provides an interesting model for chemical reactions in protein–nucleic acid complexes.

Table I. Reaction of Imidazole Derivatives with *p*-Nitrophenyl Poly U Succinate (I) at 25.0°, pH 8.5

Imidazole derivative	Concn $\times 10^5$, moles/l. of imidazole groups	$10^5 \times k^{\text{i}}_{\text{obsd}}$ sec^{-1}	$(k^{\text{i}}_{\text{obsd}} - k^{\text{i}}_{\text{solvent}})$/[imidazole groups], l. mole^{-1} sec^{-1}
None	0	1.23	...
Histidine	32	1.4	(0.006)
Imidazole	32	3.9	0.08
Imidazole	333	32	0.09
Polyvinylimidazole	3.3	103	30
	10	162	16
	33	270	8
Poly-L-histidine	33	515	...

As a suppressor for the reaction of I with poly(N-vinylimidazole), an agent was sought which at low concentration would interact with the polymer–polymer complex but would not precipitate it or cause a change in the covalent bonding. Hexadecyltrimethylammonium bromide proved to be effective. Curves for two reactions are shown in Figure 1. One, the control, was allowed to proceed to completion under the standard conditions. To the other was added at time = 160 sec sufficient hexadecyltrimethylammonium bromide to give a 1.3×10^{-5} *M* solution of the detergent.[7] Within 100 sec the rate of formation of nitrophenol fell to 0.12 that of the control. Sodium dodecyl sulfate was found to function as an "antisuppressor" in this reaction. Thus when the solution was subsequently made 1.2×10^{-5} *M* in sodium dodecyl sulfate (time = 545 sec), the rate increased to 0.65 that of the control and on further addition of the sulfate (to give a total concentration of 2.3×10^{-5} *M*) it was restored to that of the control. Sodium dodecyl sulfate did not significantly influence the reaction of polyvinylimidazole with I in the absence of the ammonium detergent. In another experiment it was found that the cycle could be repeated, that is, the reaction could be retarded, accelerated, retarded, and again accelerated by successive additions of the cationic and anionic detergents (6.8×10^{-6} *M* increments). Additional reactions of *p*-nitrophenyl poly U succinate and the role of the detergent molecules in these reactions will be discussed in the full paper.

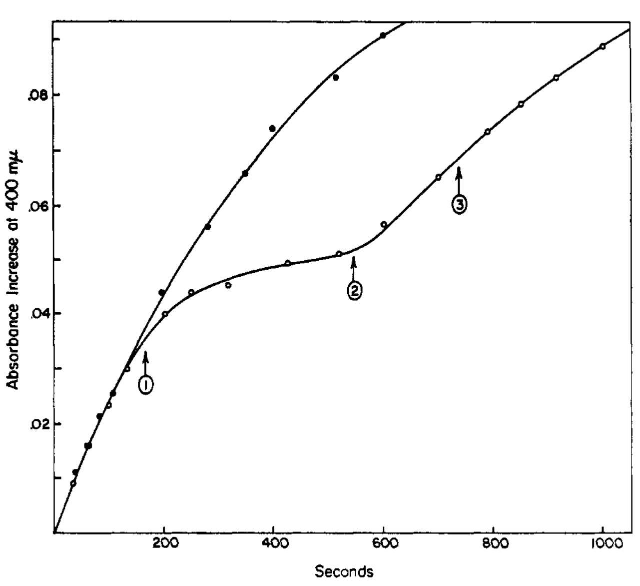


Figure 1. Regulation of rate of reaction of *p*-nitrophenyl poly U succinate (I) with poly(N-vinylimidazole): —●—control; —○— regulated reaction. (1) 0.2 cc of 2×10^{-4} *M* hexadecyltrimethylammonium bromide added to 2.8 cc of reaction mixture; (2) 0.2 cc of 2×10^{-4} *M* sodium dodecyl sulfate added; (3) 0.2 cc of 2×10^{-4} *M* sodium dodecyl sulfate added.

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(5) Kindly provided by the Badische Anilin und Soda Fabrik, Ludwigshafen, Germany.

(6) As in the polyvinylimidazole-catalyzed hydrolyses of 2,4-dinitrophenyl *p*-vinylbenzoate–acrylic acid copolymer,[1] plots of log $(A_\infty - A_0)/(A_\infty - A)$ were curved. $k^{\text{i}}_{\text{obsd}}$ represents the initial slope and satisfactorily accommodates the data through the first 30% of reaction. By 62% conversion the slope, $\Delta \log (A_\infty - A_0/A_\infty - A)/\Delta t$ was one-fourth the initial value. No precipitation occurred on mixing or during the reaction of polyvinylimidazole.

(7) This value is below the critical micelle concentration for this detergent in water or salt solutions: see T. Nash, *J. Appl. Chem.* (London), 8, 440 (1958). In another test it was found that hexadecyltrimethylammonium bromide caused polyuridylic acid to precipitate (the solution developed turbidity) in the absence of poly(N-vinylimidazole); however, no precipitation occurred when poly(N-vinylimidazole) was present in the solution with polyuridylic acid and the detergent.

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