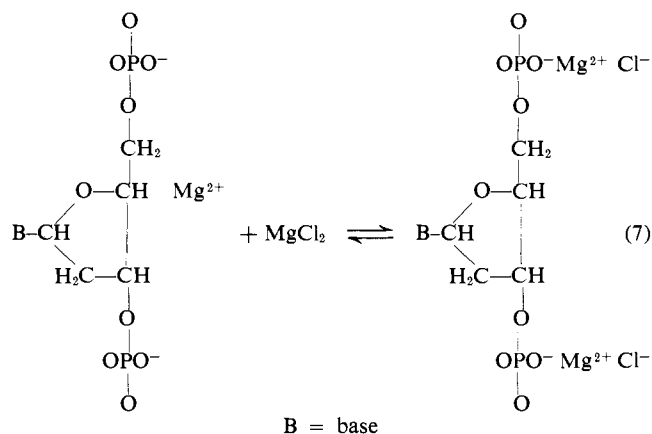


In the discussion of magnesium binding in the absence of simple salt, the unfavorable spacing of the phosphate sites in DNA was cited to explain the failure to observe appreciable site binding in the pure polyelectrolyte solution. When additional magnesium ions are added, the requirement that one magnesium ion simultaneously is to satisfy two phosphate sites no longer applies. It is suggested that the following may occur to some extent.



In the above representation the two magnesium ions in the product can be treated as site bound with the result

that the charge on this segment of the DNA is reversed; *i.e.*, viewed from the solvent, the segment now appears to be a polycation with negative univalent counterions ( $\text{Cl}^-$ ). Reports of charge reversal are by no means rare, the phenomenon having been invoked to explain reversal in sign of the electrophoretic mobility of polyvinylpyridinium bromides in excess  $\text{KBr}$ <sup>26</sup> and for colloidal ferric hydroxide in base.<sup>27</sup> Recently, a reversal of charge on the surface of  $\text{AgI}$  or  $\text{AgBr}$  colloids by addition of aluminum ions hydrolyzed to varying extents has been thoroughly studied.<sup>28</sup> Thus, eq. 7 is not unreasonable.

In a current paper,<sup>29</sup> we discuss the effect of excess  $\text{MgCl}_2$  on the secondary structure of DNA and show *via* additional experimental techniques that eq. 7 is the most plausible explanation of the binding by DNA of magnesium ions from  $\text{MgCl}_2$ .

*Acknowledgment.* The financial support of the Monsanto Co. is gratefully acknowledged.

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## Catalysis of the Dehydration Reaction of Carbonic Acid by Poly-N-vinylimidazole

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*Contribution from the Department of Chemistry of the Polytechnic Institute of Brooklyn, New York. Received October 15, 1964*

The rate of the dehydration reaction of carbonic acid at 25° was found to be catalyzed by poly-N-vinylimidazole (PVI) as measured by the Roughton thermometric continuous-flow method. The first-order rate constant in 0.001 M PVI was found to be 36.8  $\text{sec}^{-1}$  compared with 26.2  $\text{sec}^{-1}$  for the uncatalyzed reaction. The catalytic coefficient for this reaction was found to be 400 for PVI as compared with 1.5 for imidazole and 12 for 2,4-dimethylimidazole. Solutions of PVI in the presence of  $\text{Zn(II)}$  with and without nitrilotriacetic acid showed no further enhancement over that due to the polymer alone, probably owing to the low extent of complex formation in the dilute solutions investigated.

The kinetics of the reaction between carbon dioxide and water has long been of interest; it is of fundamental importance in processes of respiration and was one of the first "rapid" reactions to be studied quantitatively. This system is often used as a standard for the testing of new apparatus for measuring fast reactions.<sup>2</sup> Rate studies show that the rates of the hydra-

tion and dehydration reactions are strongly affected by buffers,<sup>3,4</sup> with anionic activation the predominant effect.<sup>3,5</sup> More recent studies by Eigen, Kustin, and Maass<sup>6</sup> on a more general reaction scheme have been followed by the work of Ho and Sturtevant<sup>7</sup> and Gibbons and Edsall,<sup>8</sup> who evaluated these rate constants. No known synthetic catalyst compares in effectiveness with the enzyme carbonic anhydrase, a zinc-containing protein.<sup>9-12</sup> The structure of the complex is unknown; a 4s4p<sup>3</sup> complex of  $\text{Zn(II)}$  in carbonic anhydrase has been postulated.<sup>13</sup> Edsall and Wyman<sup>14</sup> have written an excellent review of the chemistry, particularly of the kinetics of the reactions of carbon dioxide and carbonic acid.

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This laboratory has been studying several metal-polyelectrolyte complexes in solution. Because of the importance of the imidazole moiety in biochemical processes, the properties of poly-N-vinylimidazole (PVI)<sup>15, 16</sup> and its complexes with metals<sup>17</sup> have received special attention. Recent studies have elucidated the nature of the complex of PVI with Zn(II).<sup>18</sup> This contribution is a report of the catalytic effects of PVI and its Zn(II) complex on the kinetics of the dehydration reaction of carbonic acid.

### Experimental

The kinetics of the dehydration reaction as catalyzed by PVI, complexes of PVI and Zn(II), and mixed complexes of the latter two substances with nitrilotriacetic acid (NTA) were studied using the Hartridge-Roughton thermometric continuous-flow system. For experimental details not presented herein, the thesis should be referred to.<sup>1</sup> PVI was obtained through the courtesy of Badische Aniline und Soda Fabrik. Its weight-average molecular weight was estimated to be 138,000 by light-scattering measurements. The general properties and purity of this material have been described previously.<sup>15, 16</sup> Stock solutions were prepared by weight and their titer determined potentiometrically with standard acid. All concentrations are expressed as base moles per liter. Solutions of hydrochloric acid and sodium bicarbonate were prepared and standardized by usual analytical procedures. A stock solution of zinc(II) nitrate (analytical reagent) which was 0.2 *M* in this salt and 0.005 *M* in nitric acid to prevent hydrolysis was diluted as required; its Zn(II) titer was established by EDTA titration.<sup>19</sup> The nitrilotriacetic acid (NTA) stock solution was prepared from freshly dried reagent grade stock. Its concentration was determined spectrophotometrically with a standardized copper(II) solution at 734 m $\mu$ .

Several experimental methods have been employed to follow the rapid dehydration reaction of carbonic acid and to evaluate the effectiveness of different catalytic systems. In order to avoid the effects of extraneous factors, e.g., light, indicator dye, electric current, etc., upon the reaction, we chose the thermometric method and a continuous-flow system.<sup>20</sup> The flow system was immersed in a well-stirred water thermostat, with the temperature controlled to  $\pm 0.001^\circ$  (Bayley Instrument Co. Model 95 precision temperature controller). An auxiliary constant heater controlled by a Variac was also used to reduce the load on the temperature-control relay system.

The thermocouple had a single pair of junctions, one of which was mounted on a cathetometer and inserted in the streaming fluid with the reference junction in an insulated tube immersed in the thermostat. The copper and constantan wires of the thermocouple (30 gauge, Leeds and Northrup) were insulated with Bakelite varnish. The thermocouple was connected to a

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Keithley Model 149 millimicrovoltmeter, the output of which was fed to a Leeds and Northrup Speedomax Type G recorder.

The actual procedure was as follows. The 2-l. reagent bottles were filled with solution A (hydrochloric acid) and B (sodium bicarbonate, with or without catalyst). These were connected through remotely controlled stopcocks to a mixing chamber fed by four tangential jets, each 1 mm. in diameter. The chamber led directly to a 2-mm. i.d. vertical observation tube, which in turn was connected to a sample collection chamber. The diameter and uniformity of the observation tube were determined by direct calibration with mercury. Temperature equilibrium of the system was attained within 2 hr. The thermojunction was then placed at a suitable position in the observation tube, compressed nitrogen was applied to bottles A and/or B, and e.m.f. readings were taken with the flow of fluid A (or B) alone, then with A and B together, and finally with B (or A) alone. The flow rate was calculated by measuring the flow time and the collected volume of fluid during this period. A typical flow rate in the observation tube was 250 cm. sec.<sup>-1</sup>. Immediately after each reaction, samples of A, B, and their reaction mixture (M) were analyzed by direct titration. The relative rates of delivery of A and B were then calculated. If  $A'$ ,  $B'$ , and  $M'$  are the corresponding thermocouple readings for the flow of A and B separately and of the mixture, respectively, and  $X$  is the relative volume of A to B in the mixture, then the temperature change owing to the chemical reaction plus the heat of dilution was  $\Delta t = M' - (XA' + B')/(X + 1)$ . The neglect of the heat of dilution term does not lead to a significant error in the determination of the rate constant.<sup>20</sup> About 1 l. of each solution was consumed for each measurement.

Calibration experiments were performed by mixing water with water to give a zero heat of reaction and by mixing hydrochloric acid (0.04 *M*) with sodium bicarbonate (0.06 *M*) to give values which led to a calculated rate constant which could be compared with values from the literature.<sup>14</sup>

The time of the reaction from mixing to observation of the temperature rise was calculated according to  $t = \Delta h/\nu$  and  $\nu d^2\pi/4 = \Delta V/\Delta t$ , where  $t$  is the time in seconds,  $\Delta h$  the distance between the point of mixing and the thermocouple,  $\nu$  the linear rate of flow of solution,  $d$  the diameter of the observation tube, and  $\Delta V$  the total volume of mixed A and B collected in the flow time  $\Delta t$ .

An estimation of the accuracy of these experiments can be made from the response of the instruments. The sensitivity of the millimicrovoltmeter was such that 3  $\mu v$ . corresponded to 100 divisions (full scale) on the recorder, which could be read to  $\pm 0.5$  division when proper precautions were employed. Readings were usually taken in the 35–50 division range, so the potentials could be read to  $\pm 1\%$ . The thermocouple response was 45  $\mu v$ . deg.<sup>-1</sup>, so the temperature could be read to  $\pm 0.0002^\circ$ .

The dehydration of carbonic acid follows first-order kinetics,<sup>21</sup>  $\ln [H_2CO_3]_t - \ln [H_2CO_3]_0 = kt$ . Letting  $T$ ,  $T_\infty$ , and  $T_0$  represent the temperature rises due to the dehydration reaction at time  $t$ , at infinite time, and zero

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**Table I.** Rate Constants and Heats of Reaction of the Dehydration of Carbonic Acid at 25°

Solution A	Solution B	Rate constant $k$ , sec. <sup>-1</sup>	$\Delta H_1$ , cal. mole <sup>-1</sup>	$\Delta H_2$ , cal. mole <sup>-1</sup>
HCl (0.0413 M)	NaHCO <sub>3</sub> (0.0609 M)	26.2	785	1290
HCl (0.0608 M)	NaHCO <sub>3</sub> (0.0401 M)	26.2	785	1290
PVI (0.001 M)				
HCl (0.0404 M)	NaHCO <sub>3</sub> (0.0609 M)	31.4	775	1300
	PVI (0.001 M)			
HCl (0.0404 M)	NaHCO <sub>3</sub> (0.0609 M)	31.4	775	1300
	PVI (0.001 M)			
	Zn(II) ( $2 \times 10^{-6}$ M)			
HCl (0.0410 M)	NaHCO <sub>3</sub> (0.0615 M)	36.8	810	1265
	PVI (0.002 M)			
HCl (0.0400 M)	NaHCO <sub>3</sub> (0.0570 M)	31.4	775	1300
	PVI (0.001 M)			
	Zn(II) ( $1.1 \times 10^{-4}$ M)			
	N(CH <sub>2</sub> COOH) <sub>3</sub> (0.001 M)			

time, respectively, the kinetics of this process may be expressed as  $\ln(T_\infty - T) - \ln(T_\infty - T_0) = -kt$ . Plots of  $\ln(T_\infty - T)$  vs.  $t$  are shown in Figure 1 for different systems, corrected to an original carbonic acid concentration of 0.0200 M. Here  $T_\infty$  was calculated from the known over-all heat of the neutralization reaction.<sup>21</sup> The value of the ordinate at zero time ( $\ln(T_\infty - T_0)$ ) was used to calculate  $T_0$ . The error in reading temperatures can lead to a maximum error in the rate constant of but 3%. Table I lists the observed

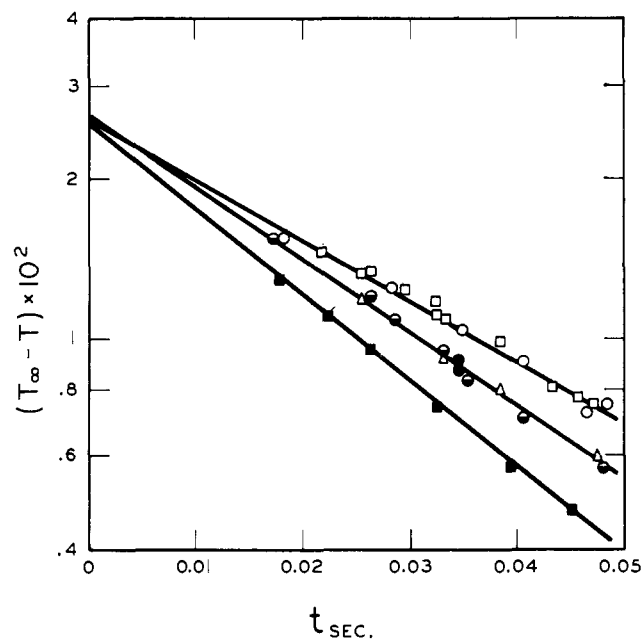


Figure 1. Rate plots for the dehydration of carbonic acid at 25°. Solutions pairs are: 0.04 M HCl and 0.06 M NaHCO<sub>3</sub> (○); 0.06 M HCl + 0.001 M PVI and 0.04 M NaHCO<sub>3</sub> (□); 0.04 M HCl and 0.06 M NaHCO<sub>3</sub> + 0.001 M PVI (◐); + 0.001 M PVI and  $2 \times 10^{-6}$  M Zn(II) (Δ); + 0.002 M PVI (■); + 0.001 M PVI,  $1.1 \times 10^{-4}$  M Zn(II), and 0.001 M N(CH<sub>2</sub>COOH)<sub>3</sub> (●).

rate constants, together with calculated values of the heat of reaction of hydrogen and bicarbonate ions ( $\Delta H_1$ ) and the enthalpy of the dehydration reaction ( $\Delta H_2$ ). Values of  $\Delta H_1$  and  $\Delta H_2$  were calculated from  $\Delta H_1 = T_0 C / [H_2CO_3]_0$  and  $\Delta H_2 = (T_\infty - T_0) C / [H_2CO_3]_0$ , where  $C$  is the specific heat of the solution. The values

for the rate constants were read off the plots of Figure 1, and it may be seen that the error here is considerably less than the 3% maximum indicated earlier. The availability of the millimicrovoltmeter employed reduced our experimental difficulties, and with more precautions even greater reliability can be attained.

### Discussion

The calculated values of  $k$  and  $\Delta H$  for the non-catalyzed reaction are quite consistent with those published in the literature.<sup>14</sup> The catalytic effects of the PVI, PVI-Zn(II), and PVI-Zn(II)-N(CH<sub>2</sub>COOH)<sub>3</sub> systems were found to be the same in these basic (pH 7.6) solutions as studied here. The Zn(II) complex or mixed complex apparently contributed no additional catalytic effect. PVI showed no catalytic effect in its protonated state in acidic solutions; it shows typical basic catalysis as described by Roughton and Booth<sup>3</sup> in their studies of the effects of simple buffers.

The catalytic effect of PVI (and of its complexes) was evaluated according to  $\text{rate}_{\text{obsd}} = k_{\text{obsd}}[H_2CO_3] = k_0\{1 + \lambda[B]\}[H_2CO_3]$  where  $\text{rate}_{\text{obsd}}$  is the observed dehydration rate of carbonic acid in a buffer,  $k_{\text{obsd}}$  is the observed rate constant,  $[B]$  is the concentration of the basic constituent of the buffer,  $k_0$  is the rate constant extrapolated to zero  $[B]$ , and  $\lambda$  is the evaluated catalytic coefficient. The  $\lambda$ -value of free PVI was thus evaluated to be  $400 \pm 12$ , as compared with  $\lambda = 1.5$  for imidazole.<sup>3</sup> The active site is obviously the imidazole group in both compounds; whether this enhancement is due to the presence of the functional groups on a polymeric coil and is a general phenomenon or one specific to this dehydration reaction is still an open question, pending further investigation of the effects of polyelectrolytes and their monomeric analogs. The  $pK$  of PVI is a function of its own concentration and that of the salt present; under the circumstances studied here, its value is 5.0. The value of  $\lambda$  for 2,4-dimethylimidazole is 12; although this compound is not N-substituted, it may indicate that the N-ethyl substitution in the polymer is by itself of little effect. Our experiments of the catalytic effect of the PVI-Zn complex and the PVI-Zn-nitilotriacetic acid complex were not considered definitive because only a small fraction of the polymer was in the metal complex form. For example, with  $5 \times 10^{-4}$  M PVI and  $10^{-6}$  M Zn(II),

the concentrations of the Zn(II)·PVI complex or of the Zn(II)·(PVI)<sub>4</sub> complexes were estimated to be 10<sup>-8</sup> M, too low to be of measureable effect. It is not possible to add more Zn(II) to the PVI solution to obtain a higher concentration of the complex without effecting cross linking of the polymer and subsequent precipita-

tion. Further studies on this and similar systems employing similar but stronger complexes are under way.

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## Catalytic Activity of Platinum Black. III. Adsorption and Decomposition of Butanes

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*Contribution from the General Electric Research Laboratory, Schenectady, New York. Received November 23, 1964*

*The adsorption and catalytic decomposition of n- and isobutane on sintered platinum black has been studied in the temperature range 0–180°. Below 50° physical adsorption of both butanes occurred with coverages exceeding a monolayer, but increasing amounts of irreversible chemisorption took place at higher temperatures. Above 80°, methane, small amounts of ethane, and propane were desorbed, and a carbonaceous residue was deposited on the metal surface. The extent of decomposition was greater for n-butane than for isobutane between 100 and 180°, and both cracked more readily than propane under the same conditions. The distribution of products was quite different from that observed in hydrocracking in the presence of excess hydrogen, and no isomerization was detected. The mechanism of butane decomposition is discussed, and it is suggested that the kinetics may be controlled by the rate of hydrogenation of adsorbed hydrocarbon residues.*

### Introduction

Considerable interest has recently arisen in the use of platinum black as an electrocatalyst in hydrocarbon fuel cells. In this application both dissociative adsorption of the hydrocarbon and electrochemical oxidation of adsorbed species occur at the metal surface.<sup>1</sup> However, although the rate of the catalytic decomposition of the hydrocarbon plays an important role in determining the over-all performance of the fuel cell anode, the detailed mechanism of this process is not well understood. In particular, little information is available on the extent of adsorption of hydrocarbons on finely divided metals such as platinum black at temperatures where the rate of decomposition is small.

Previous work in this series<sup>2,3</sup> was concerned with the changes that occurred in the cracking patterns of simple hydrocarbons over platinum black during the progressive sintering of the catalyst. In the case of the decomposition of propane and cyclopropane, the specific activity of the metal, or activity per square centimeter, decreased very rapidly during sintering,

suggesting that the latter process involved elimination of the active sites responsible for the hydrocarbon decomposition. The results also indicated that adsorption of the hydrocarbon preceded decomposition in every case.

The present paper describes a study of the adsorption and decomposition of normal and isobutanes in the temperature range in which the rate of cracking of the hydrocarbons was slow. It was hoped to compare the results of this work with those obtained previously on the kinetics of cracking of propane and cyclopropane<sup>2,3</sup> on an identical catalyst and with the reported results of hydrocracking of butanes on evaporated platinum films.<sup>4</sup>

### Experimental

*Materials.* The platinum black used in this work was obtained from Fisher Co. and had a chloride content less than 60 p.p.m.; it was part of the same batch used in previous investigations.<sup>2,3</sup> The unreduced black as received had a B.E.T. nitrogen surface area of 19.5 m.<sup>2</sup>/g., but, in order to eliminate sintering during the catalytic experiments, the metal was initially subjected to a standard reduction–evacuation procedure. About 0.8–0.9 g. of the black was sealed into the vacuum system, and evacuation was carried out at 150° overnight to a pressure below 10<sup>-6</sup> mm. Dry nitrogen (10 cm.) was admitted to the sample after the latter had been cooled to room temperature, and pure hydrogen was allowed to flow slowly into the catalyst chamber through a palladium membrane. The presence of nitrogen tended to decrease the initial sintering of the catalyst. Following reduction in flowing hydrogen at room temperature for 1 hr., the temperature of the sample was slowly raised to 150° over a period of 30 min., the flow of hydrogen continuing during this time. Finally, the catalyst was evacuated at 150° for several hours to a pressure below 10<sup>-6</sup> mm. This procedure was found to reduce the surface area of the black to 7–8 m.<sup>2</sup>/g., and no further changes in surface area occurred during the subsequent catalytic runs.

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