

which can account most reasonably for the observed results are  $^1\Delta_g$  or  $^1\Sigma_g$  forms of  $O_2$ . Both of these are known to be produced by the technique used in the present work,<sup>6,9,10</sup> the former in greater amount by at least  $10^2$ .

The relative rates of peroxidation of the three anthracenes studied were 9,10-dimethylantracene > 9,10-diphenylantracene > anthracene. With the particular apparatus used in the present work, 19 hr. was required for complete conversion of 100 mg. of 9,10-dimethylantracene to the 9,10-peroxide. Even in the case of this relatively reactive substrate there does not seem to be a highly efficient capture of reactive oxygen, based on the supposition that 10% of the oxygen molecules are converted to the  $^1\Delta_g$  state<sup>6</sup> and the estimated flow rate. The considerable difference in reactivity of 9,10-dimethylantracene and anthracene (roughly 100-fold) indicates that this reactive  $O_2$  is rather selective.

An interesting effect of solvent on the rate of peroxidation of 9,10-diphenylantracene was noted. Chlorobenzene, bromobenzene, and nitrobenzene gave faster reaction rates than anisole, dimethyl sulfoxide, or iodobenzene (which were all about the same), and these in turn led to faster oxidation than *p*-cymene or decalin. The rate factor from the most effective solvent chlorobenzene to decalin, the poorest, was over twenty (at 0°).

Reactive 1,3-dienes are also susceptible to endoperoxidation. For example, and in analogy with the classical case of photooxidation,<sup>3</sup> exposure of  $\alpha$ -terpinene to singlet oxygen afforded ascaridol. 2,5-Diphenyl-3,4-isobenzofuran afforded 1,2-dibenzoylbenzene<sup>3</sup> in high yield. On the other hand, attempts to convert olefins to allylic hydroperoxides have so far not succeeded in the case of  $\alpha$ -pinene, 1-phenylcyclohexene, tetramethylethylene (gas phase), or cholest-4-en-3 $\beta$ -ol. Work is in progress to ascertain the significance of these preliminary results.

Although the instrumentation and techniques used in the present work are quite simple (comparable to those conventionally employed for ozonolysis), they are satisfactory only on a limited scale; with quantities greater than several millimoles, inconveniently long reaction times are required for complete conversion. Improvements in the metastable oxygen generator are clearly desirable.

We have followed with interest several recent publications on the chemical generation of singlet oxygen by the oxidation of hydrogen peroxide,<sup>11-14</sup> but we have done no work on the application of these systems to peroxidation of organic substrates. We have been informed by Professor Christopher Foote<sup>15</sup> that he has succeeded in effecting a number of peroxidation reactions by the oxidation of hydrogen peroxide in the presence of various substrates.

(9) L. Elias, E. A. Ogryzlo, and H. I. Schiff, *Can. J. Chem.*, **37**, 1680 (1959).

(10) M. A. A. Clyne, B. A. Thrush, and R. P. Wayne, *Nature*, **199**, 1057 (1963).

(11) A. U. Khan and M. Kaska, *J. Chem. Phys.*, **39**, 2105 (1963).

(12) S. J. Arnold, E. A. Ogryzlo, and H. Witzke, *ibid.*, **40**, 1769 (1964).

(13) E. J. Bowen and R. A. Lloyd, *Proc. Chem. Soc.*, 305 (1963).

(14) R. J. Browne and E. A. Ogryzlo, *ibid.*, 117 (1964).

(15) C. S. Foote, personal communication, June 22, 1964; see C. S. Foote and S. Wexler, *J. Am. Chem. Soc.*, **86**, 3879, 3880 (1964). Professor Foote has also indicated that Professor K. Bayes of U.C.L.A. is also engaged in the study of singlet  $O_2$ .

It is possible that singlet  $O_2$  might also be a product of other types of chemical processes, *e.g.*, the reaction of hydrogen peroxide with oxalyl chloride,<sup>16</sup> which yields both molecular oxygen and luminescence, and the reactions of ozone with phosphines, phosphite esters, sulfides, etc.<sup>17</sup>

Work on the chemistry of externally generated metastable oxygen is being continued along the lines suggested by the results described above.

**Acknowledgment.**—We thank the National Science Foundation for financial support under Grant GP-221 and Professors William Klemperer and Dudley Hershbach for helpful discussions.

(16) E. A. Chandross, *Tetrahedron Letters*, No. 12, 761 (1963).

(17) See Q. E. Thompson, *J. Am. Chem. Soc.*, **83**, 845 (1961), and references cited therein.

DEPARTMENT OF CHEMISTRY  
HARVARD UNIVERSITY  
CAMBRIDGE, MASSACHUSETTS 02138

E. J. COREY  
WALTER C. TAYLOR

RECEIVED JUNE 25, 1964

### Amineborane Reductions in Aqueous Acid Media

Sir:

Recent solvolysis studies<sup>1,2</sup> have shown that certain amineboranes have a high degree of kinetic stability in water and mixed aqueous solvents. Their slow rates of hydrolysis permit studies of their reactions in highly acidic media, conditions which preclude the study of many other hydridic compounds such as the alkali metal borohydrides. The present communication describes an investigation of reactions of amineboranes with specific carbonyl compounds under such conditions. The amineboranes employed were effective reducing agents in strong aqueous acid, and *their rates of reaction with carbonyl compounds were found to increase with increasing acidity of the medium.*

The use of amineboranes for the reduction of aldehydes and ketones to the corresponding alcohols is well known.<sup>3-7</sup> In the present investigation, the rate of disappearance of each amineborane in a buffered solution containing a large excess of the carbonyl compound was followed iodometrically<sup>8</sup> and found to be first order in amineborane. Variations in rate with changes in the concentration of the carbonyl component revealed a first-order dependence on the concentration of aldehyde or ketone. For a given system, above a certain concentration of hydrogen ion, the observed rate varied linearly with  $[H^+]$  as shown in Fig. 1 for the reaction of acetone with morpholineborane in water at 25°. The data lead to the following rate equation.

$$-\frac{d(\text{amineborane})}{dt} = (\text{amineborane}) \left( R-\overset{\text{O}}{\parallel}{C}-R' \right) (k_1 + k_2[H^+])$$

(1) H. C. Kelly, F. R. Marchelli, and M. E. Giusto, *Inorg. Chem.*, **3**, 431 (1964).

(2) G. E. Ryschkewitsch, *J. Am. Chem. Soc.*, **82**, 3290 (1960).

(3) Callery Chemical Co., Technical Bulletin C-200, April, 1958.

(4) R. P. Barnes, J. H. Graham, and M. D. Taylor, *J. Org. Chem.*, **23**, 1561 (1958).

(5) H. Nöth and H. Beyer, *Ber.*, **93**, 1078 (1960).

(6) W. M. Jones, *J. Am. Chem. Soc.*, **82**, 2528 (1960).

(7) H. C. Kelly and J. O. Edwards, *ibid.*, **82**, 4842 (1960).

(8) D. A. Lyttle, E. H. Jensen, and W. A. Struck, *Anal. Chem.*, **24**, 1843 (1952).

TABLE I

EFFECT OF HYDROGEN ION CONCENTRATION ON THE RATES OF REACTION OF AMINEBORANES WITH CARBONYL COMPOUNDS AT 25°

I. Morpholineborane + <i>p</i> -hydroxybenzaldehyde in 50% dioxane-50% water						
[H <sup>+</sup> ] <sup>b</sup>	10 <sup>-7</sup>	9 × 10 <sup>-8</sup>	4.3 × 10 <sup>-4</sup>	1.65 × 10 <sup>-3</sup>	5.6 × 10 <sup>-3</sup>	
<i>k</i> <sub>obsd</sub> × 10 <sup>3</sup>	0.198	0.223	0.303	0.738	2.10	
II. Morpholineborane + acetone in water						
[H <sup>+</sup> ]	<10 <sup>-8</sup>	1.7 × 10 <sup>-4</sup>	2.8 × 10 <sup>-4</sup>	3.5 × 10 <sup>-4</sup>	6.8 × 10 <sup>-4</sup>	1.16 × 10 <sup>-3</sup>
<i>k</i> <sub>obsd</sub> × 10 <sup>3</sup>	0.11	0.18	0.23	0.266	0.392	0.582
III. N-Methylmorpholineborane + 2-methylpropanal in water						
[H <sup>+</sup> ]		2.6 × 10 <sup>-6</sup>		2.2 × 10 <sup>-4</sup>		5.7 × 10 <sup>-4</sup>
<i>k</i> <sub>obsd</sub> × 10 <sup>3</sup>		0.193		1.17		2.60
IV. N-Methylmorpholineborane + acetophenone in 50% CH <sub>3</sub> OH-50% H <sub>2</sub> O						
[H <sup>+</sup> ]		~10 <sup>-7</sup>	0.06		0.09	0.12
<i>k</i> <sub>obsd</sub> × 10 <sup>3</sup>		0.004	0.38		0.53	0.83, 0.85 <sup>d</sup>
V. N-Methylmorpholineborane + <i>p</i> -methoxyacetophenone in 50% CH <sub>3</sub> OH-50% H <sub>2</sub> O						
[H <sup>+</sup> ]		~10 <sup>-7</sup>	0.09		0.12	0.17
<i>k</i> <sub>obsd</sub> × 10 <sup>3</sup>		0.007	0.23		0.30	0.43
VI. Trimethylamineborane + acetone in 50% dioxane-50% water						
[H <sup>+</sup> ]		10 <sup>-8</sup>	0.12			
<i>k</i> <sub>obsd</sub> × 10 <sup>3</sup>		0.008	6.8			

<sup>a</sup> *k*<sub>obsd</sub> = *k*<sub>1</sub> + *k*<sub>2</sub>[H<sup>+</sup>]; values were obtained by measuring the rate of disappearance of amineborane in the presence of a large excess of carbonyl compound. <sup>b</sup> Molar concentration. <sup>c</sup> Values in sec.<sup>-1</sup>. <sup>d</sup> Obtained by measuring the rate of disappearance of ketone in the presence of a large excess of amineborane.

Rates of reduction of selected aldehydes and ketones at 25° are shown in Table I. In these studies, the initial concentration of amineborane varied from about 3 × 10<sup>-3</sup> to 10<sup>-2</sup> *M*. Buffer solutions were prepared using mixtures of potassium acid phthalate and either hydrochloric acid or sodium hydroxide for studies at hydrogen ion concentrations ranging from about 10<sup>-2</sup> to 10<sup>-6</sup> *M*. Aqueous HCl was used in solutions where [H<sup>+</sup>] exceeded 0.05 *M*. Initial concentrations of carbonyl compound ranged from about 0.06 to 0.81 *M*. Over the entire reported range of acidity, the rate of loss of soluble hydride in the absence of carbonyl compound was negligible compared to the rate of reduction of the carbonyl compound. Thus, hydrolysis of the amineborane was not significant under these conditions. In one experiment, the rate of disappearance of acetophenone (initial concentration ~0.01 *M*) in 50% aqueous methanol containing 0.12 *M* hydrogen ion and 0.21 *M* N-methylmorpholineborane at 25° was followed spectrophotometrically. Dividing the resultant pseudo-first-order rate constant by the amineborane concentration gave a *k*<sub>obsd</sub> value within experimental error of the value obtained by measurement of the rate of loss of amineborane in the presence of excess acetophenone at the same acidity. Under these conditions, therefore, the rate of loss of N-methylmorpholineborane equals that of acetophenone.

Previous studies of the reduction of carbonyl compounds by metal borohydrides also have been found to be first order each in carbonyl compound and in hydride, but no dependence of rate on acidity was reported.<sup>9-13</sup> In fact, Freund and Nuenke<sup>14</sup> have reported that the reduction of acetone by sodium borohydride was not catalyzed by hydrogen ion in the pH

(9) E. R. Garrett and D. A. Lyttle, *J. Am. Chem. Soc.*, **75**, 8051 (1953).

(10) E. H. Jensen, "A Study on Sodium Borohydride," *Nyt Nordisk Forlag Arnold Busck, Copenhagen*, 1954.

(11) H. C. Brown, E. J. Mead, and B. C. Subba Rao, *J. Am. Chem. Soc.*, **77**, 6209 (1955).

(12) J. L. Mateos, *J. Org. Chem.*, **24**, 2034 (1959).

(13) W. H. Stockmayer, R. R. Miller, and R. J. Zeto, *J. Phys. Chem.*, **65**, 1076 (1961).

(14) T. Freund and N. Nuenke, *J. Am. Chem. Soc.*, **84**, 873 (1962).

region 10.2-13.0. For the amineborane reductions studied here, the acid-dependent term in the rate expression was not significant in solutions of less than about 10<sup>-6</sup> *M* hydrogen ion. While the acidity of these amineborane solutions could be increased so

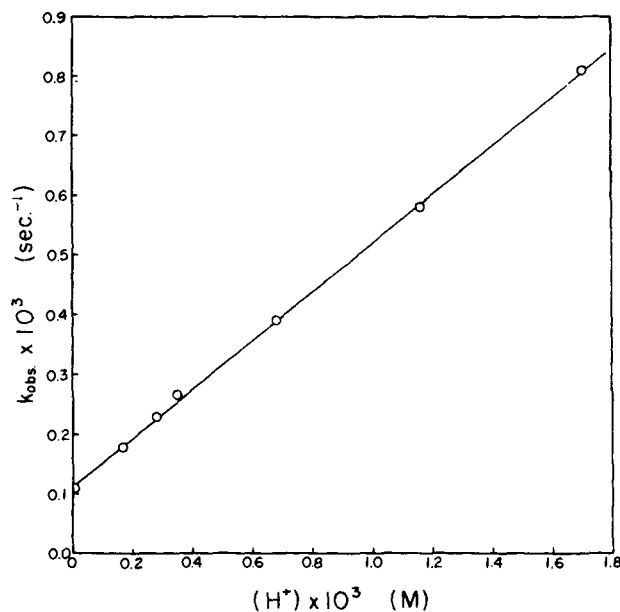


Fig. 1.—Rate of reaction of acetone with morpholineborane in water at 25° vs. [H<sup>+</sup>].

that a dependence of hydrogen ion on the reaction rate could be observed without significant loss of hydride due to hydrolysis, the relatively rapid rate of hydrolysis of sodium borohydride has complicated efforts to establish whether reduction of carbonyl compounds by this reagent exhibits hydrogen ion dependence at low pH.

The dependence of the amineborane reaction rate on hydrogen ion concentration may be due to the formation of a protonated carbonyl species from the hydrogen ion and the aldehyde or ketone in a rapid equilibrium, followed by a rate-determining step involving attack

of amineborane on the neutral or protonated carbonyl compound with the latter being favored. Possibly the reaction with amineborane is enhanced by factors, such as protonation, which increase the electron-deficient character of the carbonyl carbon atom.<sup>15</sup> These suggestions, however, are strictly speculative at this time. It should be noted that the reactions described herein proceed with the evolution of H<sub>2</sub> gas and therefore differ in stoichiometry from the reported reduction of monofunctional carbonyl compounds, such as acetone, with sodium borohydride. Factors influencing the stoichiometry of these reactions are being investigated, as are isotope and substituent effects on rates.

The high kinetic stability of these amineboranes suggests that they may become quite useful as hydridic reagents in aqueous acid. Although certain reductions proceed slowly in neutral or alkaline solution, the effect of acid in enhancing reaction rates provides a means for extensive practical use of amineboranes in the reduction of carbonyl compounds in water and mixed aqueous solvents.

**Acknowledgment.**—The authors wish to thank Mr. A. A. Hinckley for helpful discussions.

(15) Attack by amineborane at an electron-deficient center has been proposed to explain the increase in rate of reduction of cyclohexanone by various amineboranes in tetrahydrofuran with added H<sub>2</sub>SO<sub>4</sub> or anhydrous HCl: see L. Murray, Ph.D. Thesis, Purdue University, Jan., 1963.

(16) Correspondence should be addressed to the Department of Chemistry, Texas Christian University, Fort Worth, Texas.

CHEMICAL RESEARCH AND  
DEVELOPMENT LABORATORIES  
METAL HYDRIDES INC.  
BEVERLY, MASSACHUSETTS

HENRY C. KELLY<sup>16</sup>  
MARIO B. GIUSTO  
FRANK R. MARCHELLI

RECEIVED JULY 10, 1964

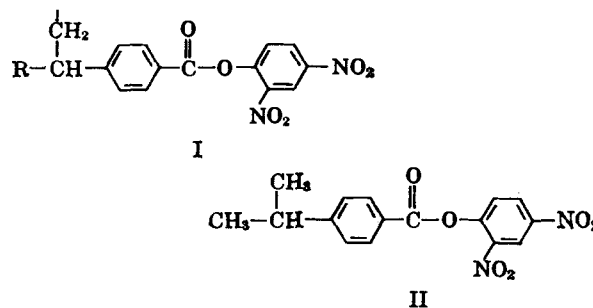
### Selective Catalysis Involving Reversible Association of a Synthetic Polymeric Catalyst and Substrate<sup>1</sup>

Sir:

The high degree of substrate specificity exhibited by many enzymes is attributable, in part at least, to a specific binding of the substrate to the enzyme. Attempts to develop homogeneous systems of synthetic substances which exhibit selective catalytic features similar to those characterizing the enzymatic systems have met with only limited success. The best examples appear to be the solvolysis of substituted nitrophenyl acetates catalyzed by partially protonated poly(4-vinylpyridine),<sup>2</sup> poly(N-vinylimidazole),<sup>2</sup> and poly(4(5)-vinylimidazole).<sup>3</sup> In these cases substrates bearing a negatively charged substituent group exhibited unusually high reactivity, presumably as a consequence of electrostatic attraction between the substrate and catalyst.<sup>4</sup>

We now report results of an investigation of the solvolysis of copoly(acrylic acid-2,4-dinitrophenyl *p*-vinylbenzoate) (I) catalyzed by partially protonated

poly(N-vinylimidazole).<sup>5</sup> This polymer system exhibits a number of features of enzymatic reactions not found with the synthetic substances previously studied<sup>2,3</sup> and provides kinetic evidence for association of the catalyst with the substrate.



R contains -CH<sub>2</sub>CH-COOH

Copolymer I ( $\eta$  0.09; 62% by weight dinitrophenyl vinylbenzoate) was prepared by polymerizing acrylic acid and 2,4-dinitrophenyl *p*-vinylbenzoate in benzene. Solvolyses were conducted in 50% (w./w.) ethanol-water at pH 7.5<sup>6</sup> and  $25.0 \pm 0.1^\circ$  in a cuvette in a Beckman DU spectrophotometer, formation of 2,4-dinitrophenol being followed by the increase in absorbance at 412 m $\mu$ .

Satisfactory pseudo-first-order kinetics were obtained for 2,4-dinitrophenyl *p*-isopropylbenzoate; however, curvature in the plots of  $\log(A_\infty - A)$  vs. time for the reaction of copolymer I was found.<sup>7</sup> In treating the data for I it was convenient to use the empirical relation<sup>8</sup>

$$(A - A_0)/(A_\infty - A) = k't$$

As shown in Fig. 1, a reasonably good fit to this equation was obtained for solvolyses conducted in the absence of active nucleophilic catalysts as well as in those catalyzed by N-methylimidazole and poly(N-vinylimidazole).

Rate data for a series of reactions in which the catalyst concentration was varied are presented in Fig. 2. With polyvinylimidazole good activity was found when the imidazole unit concentration was low ( $5 \times 10^{-4}$  M). Moreover, the rate attained a limiting value at high catalyst concentrations. For experiments in which the concentration of copolymer I was varied, a plot of the rate,  $(k' - k'_{\text{solvent}})$ (initial concentration of ester groups), as a function of the initial ester concentration afforded a similarly shaped curve (Fig. 3). Both results are explicable on the basis that copolymer I and poly(N-vinylimidazole) associate in solution and that catalysis is highly efficient in the complex that is pro-

(5) Polyvinylimidazole was supplied by the Badische Anilin und Soda Fabrik, Ludwigshafen A. Rhein, Germany.

(6) This value was selected since clear solutions, free of turbidity, were obtained on mixing the polymeric substrate and catalyst (turbidity developed on mixing at pH 7 or lower) and the pH-rate profile exhibited a maximum at this value. All solutions were 0.01 M in potassium chloride and 0.02 M in 2,4,6-trimethylpyridine. That the spectral change was due to solvolysis was shown by repeatedly scanning the spectrum from 290 to 400 m $\mu$  in a Cary spectrophotometer as the reaction proceeded. The final spectrum was that of 2,4-dinitrophenol, and an isosbestic point occurred at 313 m $\mu$ .

(7) Observation of complex kinetics in hydrolysis of functional groups on polymer chains is not uncommon. See, for example, J. Moens and G. Smets, *J. Polymer Sci.*, **23**, 931 (1957), and E. Gaetjens and H. Morawetz, *J. Am. Chem. Soc.*, **83**, 1738 (1961).

(8) " $k$ " may be considered to be a pseudo-first-order rate constant defined by the expression  $-dC/dt = k'C(C/C_0)$ , where  $C/C_0$  represents the relative reactivity of the ester groups on a polymer chain as a function of extent of reaction.

(1) This research was supported by the National Science Foundation. It benefited also from a Public Health Service training grant (5T1-GM-626) from the National Institute of General Medical Science, Public Health Service.

(2) R. L. Letsinger and T. J. Savereide, *J. Am. Chem. Soc.*, **84**, 114 (1962); **84**, 3122 (1962).

(3) C. G. Overberger, T. St. Pierre, N. Vorchheimer, and S. Yaroslavsky, *ibid.*, **85**, 3413 (1963).

(4) In addition, H. Morawetz and J. A. Shafer, *Biopolymers*, **1**, 71 (1963), have described a case in which reactivity of a cationic ester is reduced as a result of association with a polyanion.