

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF THE UNIVERSITY OF PENNSYLVANIA]

Catalytic Surfaces and the Hydrolysis of Diethyl Carbonate¹

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The heterogeneous catalysis of the hydrolysis of diethyl carbonate was studied as a diagnostic method for the characterization of solid surfaces. The kinetics of the reaction, however, did not prove to be a measure of surface basicity as anticipated from its marked specificity toward basic catalysis in solution. The ability of a solid to catalyze the reaction appeared to be related to its tendency to dissociate adsorbed water molecules, and this was shown to be a general property of ionic surfaces. To facilitate the kinetic analysis a method was devised for evaluating true activation energies and frequency factors. A mechanism of the Langmuir-Hinshelwood type is proposed, in which the critical complex is formed by reaction of adsorbed ester molecules with hydroxyl ions.

Introduction

One of the fundamental problems in the study of reactions catalyzed by solid surfaces is the devising of methods for the characterization of such surfaces in terms of directly measurable quantities. This paper describes an attempt to utilize as a diagnostic method a reaction which has been studied in solution.

The hydrolysis of diethyl carbonate, which has been studied in solution² and was shown to be rapid in the presence of bases and immeasurably slow in the presence of acids, was chosen in the hope that it would provide a direct catalytic test of the acidity or basicity of surfaces, which could then be compared with the results, for example, of Walling³ and of Mills, Boedeker and Oblad⁴ on the relationship between acidity and activity of cracking catalysts. This reaction is, furthermore, convenient to follow since the rate of evolution of carbon dioxide can be readily measured. The reaction was found to be substantially irreversible, complete conversions of ethyl carbonate actually being observed. This agrees with a value of K_p estimated from thermodynamic data at about 10^4 in atmospheres at 25°.

The results of this study display, however, no clear relationship between catalytic activity and any reasonable measure of basicity, but indicate rather that the ability to dissociate adsorbed water molecules is a sufficient qualification for activity. This ability is characteristic of ionic surfaces.

Experimental

Apparatus.—A flow system was used. Diethyl carbonate and water were pumped by separate metering pumps through an evaporator packed with copper shot into the catalyst tube. The latter consisted of a 1.3-cm. glass tube enclosed in a furnace with three independently adjustable resistance windings. Temperature control of the catalyst bed was accomplished by a phase-shifting circuit, the sensitive element being a fine platinum wire wound around the tube over the center section containing the catalyst. Temperatures were measured by a chromel-alumel couple located in a well passing through the center of the reaction tube. By suitable adjustment of resistances shunting the furnace windings above and below the catalyst section it was possible to maintain the temperature of the catalyst uniform and constant to $\pm 1^\circ$.

(1) Based on the thesis of R. W. Sauer, presented to the Faculty of The Graduate School of the University of Pennsylvania in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(2) M. H. Palomaa, E. J. Salmi and K. Suoja, *Ber.*, **72B**, 313 (1939); A. Skrabal and M. Baltadschiewa, *Monatsh.*, **45**, 95 (1924); A. Skrabal, *ibid.*, **38**, 305 (1917).

(3) C. Walling, *This Journal*, **72**, 1164 (1950).

(4) C. A. Mills, E. R. Boedeker and A. C. Oblad, *ibid.*, **72**, 1554 (1950).

The products of reaction were freed of vapors by passage through water-cooled condensers and an ice-trap, and the carbon dioxide evolved was measured either by liquid displacement or by a wet test meter.

Pressures on the inlet side of the catalyst bed were measured by a mercury manometer through a capillary bleeder, and were found to be uniformly about 15 mm. above atmospheric. The same bleeder was used to introduce carbon dioxide in some experiments.

Gaseous products from several runs were analyzed to detect possible side reactions. No ethylene was found, but at the higher temperatures up to 3% of gases not absorbed in bromine water or potassium hydroxide were noted. These were probably hydrocarbons produced by cracking since some carbon was observed to collect in the evaporator. The amount was not sufficient to affect the results.

Catalysts and Reagents.—Most of the unsupported oxide catalysts were prepared by the thermal decomposition of the nitrates. For these catalysts, J. T. Baker Analyzed $Mg(NO_3)_2$, $Cd(NO_3)_2$, $Ni(NO_3)_2$ and $Zn(NO_3)_2$, Merck and Co., Inc., Reagent Grade $Cu(NO_3)_2$, Mallinckrodt Analytical Grade $Pb(NO_3)_2$ and C.P. $Be(NO_3)_2$ were used without further purification. The Cr_2O_3 catalyst was prepared by the thermal decomposition of Merck Reagent Grade $(NH_4)_2Cr_2O_7$. The MgO catalyst was ignited overnight at 1100° and the others overnight at 600°. This treatment converted PbO to the yellow form. The oxides were then pelleted, reduced to 16/20 mesh by grinding, and re-ignited as before.

γ -Alumina was Alcoa grade F-10; boehmite was a portion of a material designated in this Laboratory as AW-3; silica gel was obtained from the Davison Chemical Corporation.

The silica-alumina catalysts were obtained from the Socony-Vacuum Oil Company and Houdry Process Corporation. These catalysts were ground to 16/20 mesh and heated in a muffle furnace at 550° for six hours before use.

The supported catalysts were prepared from analytical grade reagents by impregnation of 16/20 mesh support with an aqueous solution containing 0.0002 mole of salt per cc. of support, followed by evaporation to near dryness, with stirring, over a burner and drying at 110° for several hours.

The carbon support was prepared by grinding Columbia grade CXA activated carbon to 16/20 mesh. This carbon is reported to have a high surface area and a low ash content consisting mainly of silica. The total ash was found to be 1.27%. Carborundum was silicon carbide from Union Carbide and Carbon Company ground to 16/20 mesh.

Lead oxide and cadmium oxide on carbon were prepared by hydrolysis of the supported chlorides with water vapor in the reaction tube at 350 and 250°, respectively. The hydrolysis was assumed to be complete when the condensate no longer gave a precipitate with silver nitrate. Lead chloride used in the above preparation was made from analytical grade lead nitrate and hydrochloric acid by precipitation followed by one recrystallization from water.

Diethyl carbonate, obtained from the Mathieson Chemical Corporation, was purified by distillation (b.p. 125.8°).

Carbon dioxide, Pure Carbonic, Inc., 99.5% pure, was used without further purification.

Several other substances that might have provided examples of inactive catalysts were considered and rejected because they would have been unstable under the reaction conditions. For example, most metal sulfides would hydrolyze; many metals and alloys would react with water vapor; compounds of noble metals would be reduced.

When an attempt was made to prepare supported silver chloride from the nitrate the latter was reduced by the support. Cadmium iodide volatilized from the reaction chamber and cadmium and lead chlorides hydrolyzed.

Results and Discussion

Figure 1 shows schematically the reaction rates obtained for some of the carbon supported catalysts plotted as a function of temperature. The activity of the support is not commensurate with its high surface area and the activity of the impregnated catalysts, and it is probable that the activity of the carrier is a result of impurities and not a property of the carbon surface itself.

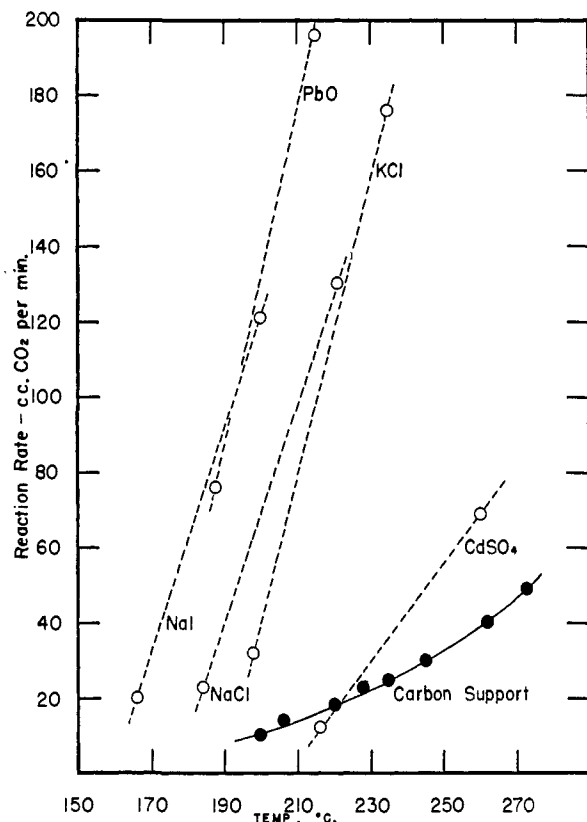


Fig. 1.—Reaction rate as a function of temperature. Approximate liquid flow rates; water 1 ml./minute, ethyl carbonate 1.3 ml./minute; catalyst volume, 10 cc.

Figure 2 shows the reaction rate plotted as a function of temperature for cadmium chloride supported on carbon. The catalyst was initially inactive, the activity increasing rapidly as the temperature was raised. Upon lowering the temperature the activity decreased, but remained at a level considerably higher than the initial rate. The increased activity coincided with the hydrolysis of cadmium chloride under the experimental conditions as determined by testing the condensate for chloride with silver nitrate. Hydrolysis occurred rapidly at 190°, and was complete in less than 15 hours. Similar results were obtained for lead chloride supported on carbon. These results suggest that cadmium and lead chlorides are poor catalysts for the reaction as compared, for example, to barium chloride and the alkali halides.

Choosing reaction rates greater than those for the carbon support as a criterion for activity re-

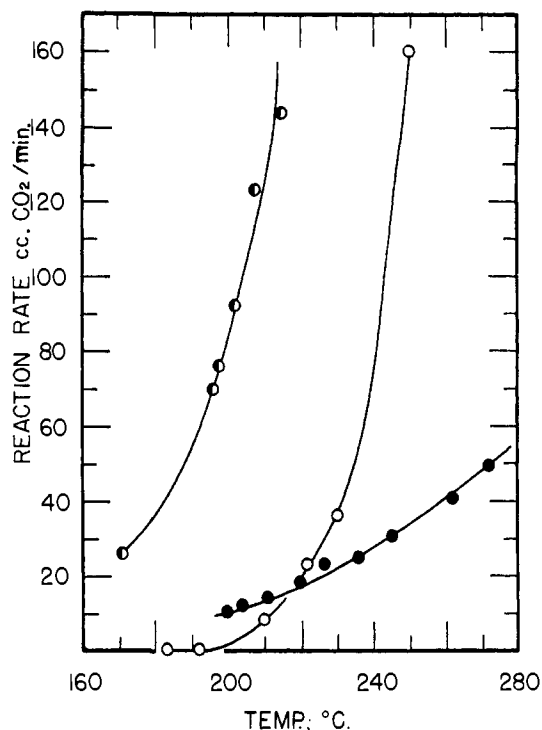


Fig. 2.—Reaction rate as a function of temperature for cadmium chloride on carbon: O, increasing temperatures; ●, decreasing temperatures; ●, carbon support. Approximate liquid flow rates: water 1 ml./minute, ethyl carbonate 1.2 ml./minute; catalyst volume, 10 cc.

sulted in the qualitative classification of catalysts shown in Table I. Some of these catalysts were selected for quantitative study as reported in the discussion to follow. Others were not studied further either because of instability or because it was believed that the results would not contribute to the general correlation. The list of effective catalysts shows no relation to the catalytic specificity toward bases characteristic of the reaction in solution. Salts of strong acids are as effective as oxides and salts of weak acids. Ionic character, however, is common to the active, partially or wholly non-ionic to the inactive substances. The appearance of lead and cadmium chlorides in the inactive class parallels their tendency toward covalent bond formation as demonstrated by low electrolytic conductivity and a tendency toward complex formation. The very weakly acidic properties of silica gel indicate a high degree of covalency in the gel structure.

TABLE I

Active catalysts		Inactive catalysts	
Unsupported	Supported on carbon	Unsupported	Supported on carbon
γ -Al ₂ O ₃	LiCl	C	PbCl ₂
Al ₂ O ₃ ·H ₂ O	NaF	SiC	CdCl ₂
SiO ₂ -Al ₂ O ₃	NaCl	Cu	
BeO	NaBr	Silica gel	
ZnO	NaI		
NiO	KCl		
CuO	BaCl ₂	FeSO ₄	
CdO	NaOAc	ZnSO ₄	
PbO	Na ₂ CO ₃	CdSO ₄	
Cr ₂ O ₃	BaCO ₃	CdO	
MgO	Na ₂ SO ₄	PbO	

A quantitative measure of activity was sought through the determination of activation energies. For this purpose it was necessary to obtain true heterogeneous activation energies, since factors such as fraction of surface covered and retardation due to products or poisons obscure the interpretation of apparent activation energies. In this particular problem difficulty arose because the activity of the catalysts was in some cases irreversibly affected by changes in environment, *e.g.*, temperature, water vapor concentration, and the presence of poisons. These effects required that all necessary measurements be made in one run, and that measurements be checked at appropriate stages in the procedure in order to ascertain the magnitude of irreversible changes which may have occurred.

The following method was used. For the reaction of two substances, A and B, at a solid surface with no mutual displacement, equation (1) may be applied where θ_A represents the fraction of the sur-

$$-dP_A/dt = k\theta_B(1 - \theta_P)\theta_A = \frac{k\theta_B(1 - \theta_P)b_A P_A}{(1 + b_A P_A)} \quad (1)$$

face covered by A at time t , and P_A and b_A are, respectively, the partial pressure and absorption coefficient of A. θ_B and $(1 - \theta_P)$ are functions in the Langmuir form of the partial pressure of reactant B and any retarding adsorbate. The constant k is the true heterogeneous rate constant; it represents the reaction rate when the surface of the catalyst is completely covered with the substrate molecules. If the effect of $(1 - \theta_P)$ can be shown to be negligible or eliminated, and if P_B is made large enough so that θ_B remains essentially constant for small changes in P_A , then the equation can be integrated. For a flow system it is desirable to change P to a function of x , the linear coördinate through the reaction bed, before integrating. Carrying out these operations yields equation (2).

$$(1/b_A)(\ln P_0/P) + P_0 - P = \theta_B(kL/v) \quad (2)$$

Where v is the linear velocity through the catalyst bed, P_0 and P are inlet and outlet partial pressures of A, and L is the length of the bed. Letting $L/v = 0.42/V_s$, where V_s is the space velocity and 0.42 is a factor which allows for the space in the catalyst chamber occupied by the catalyst, and rearranging yields

$$(P_0 - P)V_s/0.42 = \theta_B k - (1/b_A) \quad (2.303 V_s/0.42) \log P_0/P \quad (3)$$

Since $(P_0 - P)V_s/0.42$ and $(2.303 V_s/0.42) \log P_0/P$ are the usual expressions for zero and first order rate constants, respectively, equation (3) may be simplified by setting these quantities equal to k^0 and k^1 to give

$$k^0 = \theta_B k - (1/b_A)k^1 \quad (4)$$

If θ_B can be shown to approximate unity, then true activation energies may be obtained from the intercepts of (4) at two different temperatures. If θ_B is not unity, then the activation energy calculated from the intercepts is lower than the true value. Therefore, in order to apply equation (4) θ_B and θ_P must be known as functions of the partial pressures of B and P.

Table II lists the activation energies and frequency factors obtained by applying equation (4),

TABLE II
ACTIVATION ENERGIES AND FREQUENCY FACTORS

Group	Catalyst	E_a , kcal./ mole	$\log A$, min. ⁻¹
I ($\theta_B = 1$; $\theta_P = 0$)	BeO	20 ± 2	10.5 ± 0.8
	ZnO	17 ± 2	8.5 ± 0.8
	PbO ^a	23 ± 1	10.6 ± 0.8
	NiO ^a	18 ± 1	10.4 ± 0.5
	NaCl ^c	22 ± 2	11.5 ± 0.9
	NaI ^c	21 ± 3	11.3 ± 1.4
	KCl ^c	23 ± 1	11.8 ± 0.4
	CdSO ₄ ^c	24 ± 3	11.4 ± 1.3
	PbO ^c	21 ± 2	11.4 ± 0.9
	CdO ^c	20 ± 2	10.8 ± 0.9
II ($\theta_B = 1$; $\theta_P > 0$)	NiO ^b	62 ± 8	29 ± 4
	CdO ^b	45 ± 5	20 ± 2
	PbO ^b	27 ± 4	11.9 ± 1.6
III ($\theta_B < 1$; $\theta_P = 0$)	Cr ₂ O ₃	11 ± 1	7.4 ± 0.5

^a Unpoisoned. ^b Poisoned. ^c Supported on carbon.

using ethyl carbonate as reactant A and water as reactant B. The limits shown give maximum and minimum experimental values, not probable errors. Separate experiments on some of the catalysts in group I showed that the reaction was substantially zero order with respect to water vapor, *i.e.*, $\theta_B = 1$, and unaffected by changes in the partial pressures of ethanol and carbon dioxide, so that the energies of activation calculated are true heterogeneous energies. For chromic oxide, however, the rate was nearly first order with respect to water, *i.e.*, $\theta_B < 1$, making the calculated activation energy lower than the true energy. Distinct evidence of poisoning, *i.e.*, $\theta_P > 0$, was found for catalysts in group II, which may be summarized as follows: (1) When the reaction temperature was changed considerable time was required for the reaction rate to rise or fall to a constant value, even after temperature equilibrium had been obtained. (2) k^0 vs. k^1 plots were not reproducible. This is illustrated by Fig. 3 for lead oxide, the experimental points being numbered in the order in which they were obtained. (3) Cadmium and lead oxides were found to become inactive after use or after standing in bottles in the laboratory. The activity could be restored by steam treating above 280°. (4) Except for cadmium oxide effects (1) and (2) could be eliminated by shaking or refluxing the ethyl carbonate prior to use with a portion of the freshly ignited catalysts. The results of this treatment for lead oxide may be seen by comparing Figs. 3 and 4. Treatment of ethyl carbonate to remove poisons caused lead and nickel oxides to fall into group I, the poisoning effect for nickel oxide being most striking, as evidenced by a difference of 37 kcal. per mole between the calculated activation energies obtained with and without poisoning. With unsupported cadmium oxide the four effects characteristic of poisoning persisted after treatment of the ethyl carbonate. Poisoning was not observed for cadmium and lead oxides supported on carbon.

It thus appears that all of the ionic surfaces for which true activation energies and frequency factors were obtained are equally effective as catalysts. These values are near 21 kcal. per mole and 10¹¹ min.⁻¹, respectively.

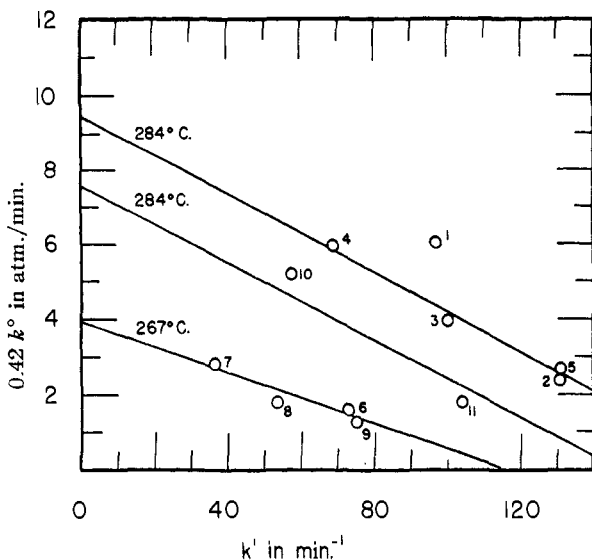


Fig. 3.—Zero order vs. first order reaction rate constants for the reaction on PbO in the presence of a catalyst poison.

Uncertainties in assigning slopes to most of the k^0 vs. k^1 plots were too great to permit a complete evaluation of heats of adsorption for ethyl carbonate, but the estimated energy of adsorption on lead oxide, 13 kcal. per mole, is indicative of the magnitude of this quantity.

For the catalysts in group I the reaction rate is independent of the water vapor concentration and proportional to the fraction of surface covered with ethyl carbonate.

The kinetic results are consistent with a mechanism which postulates a catalyst surface completely covered with strongly adsorbed, dissociated water molecules. Ethyl carbonate is moderately adsorbed on this water surface. The specificity toward alkaline hydrolysis in solution and the low proton attracting power of diethyl carbonate⁵ suggest that the first step in the formation of the activated complex involves reaction with the hydroxyl groups of the dissociated water. The absence of marked variations in the activation energy and frequency factor is evidence that the mechanism is the same for all ionic surfaces. The effectiveness of highly ionic, in contrast to partially ionic, surfaces may be attributed to the more ionic nature of the activated complex formed on the polar surfaces, since it is known that ionic resonance terms make a considerable contribution to the stability of chemical systems. The need for an ionic surface was further demonstrated by poisoning experiments in which 0.5 *M* hydrochloric acid was substituted for water. Chromium, aluminum and cadmium oxides were tested in this way, and the reaction rate was found to decrease almost to zero. The original rate was again obtained upon replacement of the hydrochloric acid with water. That this was not an "acid" effect was established by using 0.5 *M* sulfuric acid, an increase in reaction rate actually being observed. It is believed that in the experiments with hydrochloric acid metal chloride was formed on the surface, causing it to be less ionic due to the lesser electronegativity of chlorine as

(5) W. Gordy and S. C. Stanford, *J. Chem. Phys.*, **8**, 170 (1940).

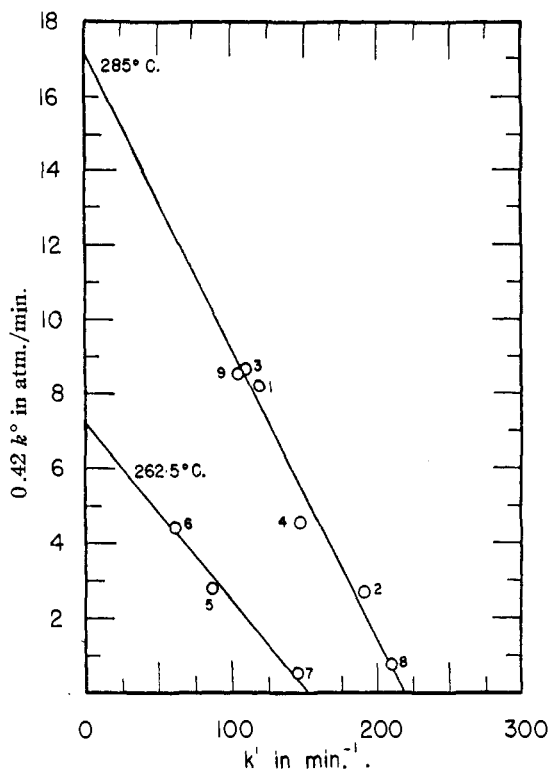


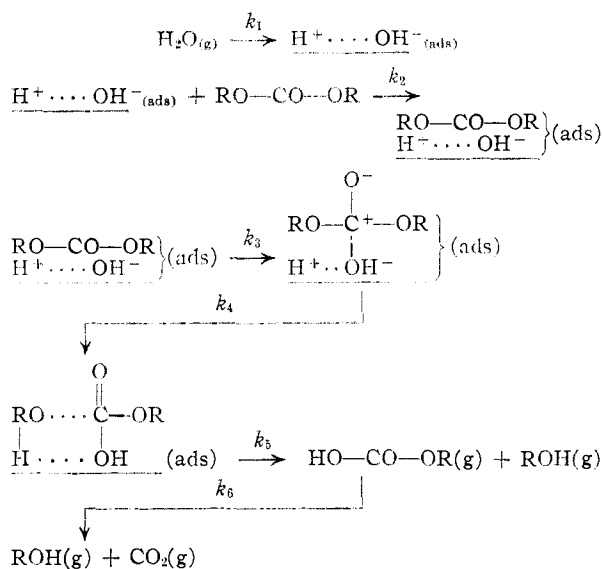
Fig. 4.—Zero order vs. first order reaction rate constants for the reaction on PbO after removal of the catalyst poison.

compared to oxygen. The relative inactivity of bulk cadmium and lead chlorides has already been mentioned, and the weak adsorption of water on chromic oxide may also be the result of reduced electronegativity differences on the surface due to the high electronegativity of chromium.

The fact that all the ionic catalysts yield similar activation energies and frequency factors is remarkable in view of their widely different physical and chemical properties. For example in the series beryllium, zinc, cadmium and lead oxides the cationic radii vary from 0.34 to 1.32 Å. with corresponding differences in the metal-oxygen distances. This series alone represents several different crystalline structures. Almost equally large differences between anionic sizes are shown in NaF and NaI.

The activated complex may be pictured as a semi-ionic system of water and diethyl carbonate polarized by the dissociative adsorption of water on an ionic surface, and the course of the reaction may be described as shown in the formulas.

It is of interest to analyze this scheme with the object of locating the rate-determining step. Since the reaction is kinetically zero order with respect to water and fractional order with respect to ethyl carbonate, the rate is evidently proportional to the area of surface on which ethyl carbonate is adsorbed over dissociated water molecules; hence k_3 , k_4 or k_5 must be rate-determining. The energy of activation for the rearrangement of the adsorbed complex would be expected to vary from surface to surface depending on the H-OH distance in the adsorbed layer and hence on the cation-anion distance in the solid. Since the true heterogeneous activation energy is independent of this dimension, it is unlikely



that k_4 is rate-determining. The desorption step k_5 may be rate-determining if the rate of desorption

of the half-ester is slow, a point which unfortunately cannot be directly tested because of the instability of this compound but, again, it would be surprising if the energy of activation for this process did not depend on the nature of the surface. Since the reaction rate is not reduced by the addition of ethyl alcohol, the desorption of this compound cannot be the limiting factor. On the whole it seems most probable that k_3 is rate-determining; and this conclusion is in concordance with observations on ester hydrolysis in solution⁶ where the overcoming of repulsive forces between water and ester was considered to be the slowest step. This result clarifies the invariance of true activation energies for catalysts chemically quite different, as it implies that the surface with which ethyl carbonate reacts is in fact simply a layer of hydroxyl ions. It is worth noting that the proposed mechanism requires that the critical complex be formed from a layer of previously adsorbed reactant.

(6) G. Davies and D. P. Evans, *J. Chem. Soc.*, 339 (1940); E. W. Timm and C. N. Hinshelwood, *ibid.*, 864 (1938).

PHILADELPHIA, PENNSYLVANIA

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Polar and Steric Substituent Constants for Aliphatic and *o*-Benzoate Groups from Rates of Esterification and Hydrolysis of Esters¹

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Parameters, E_σ , giving nearly quantitative measures of the polarities of a large number of aliphatic and *o*-benzoate substituents have been determined from rates of esterification and hydrolysis of esters. Parameters, E_s , giving nearly quantitative measures of the steric factors associated with these substituents in rates of such reactions have also been obtained. The equation, (2), used to evaluate E_σ is $(\log k/k_0)_B - (\log k/k_0)_A = E_\sigma(\rho_B - \rho_A)$, where E_σ is a substituent electron displacement (polarity) constant; ρ is a reaction constant measuring the susceptibility of the given reaction series to polar substituents; k/k_0 is the relative rate of hydrolysis or esterification for a substituent of an *o*-substituted benzoate or aliphatic ester reaction series; the subscripts A and B refer to identical acid- and base-catalyzed reaction series, resp. The basic idea involved in Eq. (2) has been previously suggested by Ingold. The equation (3) used to evaluate E_s is $\log k/k_0 = E_s + E_\sigma\rho$. Equation (3) attributes the effect of structure on rates (more properly, free energy of activation) of hydrolysis or esterification of many aliphatic or *o*-substituted benzoate esters to the sum of two distinct terms, one of steric and the other of polar origin. Evidence is given for the fact that steric factors associated with a given substituent are the same in identical acid- and base-catalyzed reaction series (so that Eq. (2) follows directly from Eq. (3)). Further, that, as a first approximation, the relative rates of acid-catalyzed hydrolysis or esterification are determined by steric factors alone, while for base-catalyzed reactions both polar and steric factors are involved. For *o*-substituted benzoates, E_σ values are found to be essentially equal to Hammett σ values for corresponding *p*-substituents. For aliphatic substituents, E_σ values are shown to be in accord with the qualitative English school theory of the polarity of groups. Corresponding E_σ values in the acyl and alkyl components of esters are found to be quantitatively parallel. The order of decreasing E_s values is that of increasing steric requirements. E_s values are not parallel in the acyl and alkyl components. E_s and E_σ values have been applied to other reactions. The logarithms of the relative rates of acid-catalyzed hydrolysis of *o*-substituted benzamides in water at 100° quantitatively parallel E_s values. The logarithms of the relative rates of hydrolysis of a series of formaldehyde acetals and the logarithms of the relative ionization constants of *o*-substituted benzoic acids in water at 25° quantitatively parallel corresponding E_σ values. For aliphatic carboxylic acids such a parallelism in general is only qualitative.

The English school has developed over a period of years a comprehensive theory of the general polarity of substituents.² However, the work of Brown, Hammett and others has emphasized the importance of steric strains, entropy and solvation effects in determining relative reactivity³ and has

(1) R. W. Taft, Jr., *THIS JOURNAL*, **74**, 2729 (1952).

(2) W. A. Waters, "Physical Aspects of Organic Chemistry," D. Van Nostrand Co., Inc., New York, N. Y., 1950, Chapter XI.

(3) (a) H. C. Brown and G. K. Barbaras, *THIS JOURNAL*, **69**, 1137 (1947); (b) H. C. Brown, R. S. Fletcher, and R. E. Johannesen, *ibid.*, **73**, 217 (1951); (c) I. Dostrovsky, E. D. Hughes and C. K. Ingold, *J. Chem. Soc.*, 173 (1946); (d) F. P. Price and L. P. Hammett, *THIS JOURNAL*, **63**, 2387 (1941); (e) T. I. Crowell and L. P. Hammett, *ibid.*, **70**, 3444 (1948); (f) P. M. Dunbar and L. P. Hammett, *ibid.*, **72**, 109 (1950).

indicated that in a number of types of reactions the polar effect plays little, or at least a minor, role. In the aliphatic series, no reaction series has yet been rigorously shown to have relative reactivities which depend only upon the polar effect of substituents so that a quantitative scale of polarities of such groups has been in doubt. The establishment of an acceptable method of evaluating polar effects is of great importance to the problem of determining the relative contributions of polar and steric factors in aliphatic reactions, and to a more complete understanding of the nature of structural factors affecting chemical reactivity.

The present subject is intended to give support