TABLE I

THE REACTIONS OF SILANE WITH ORGANOMETALLIC COMPOUNDS

Reactant with silane	Mol. ratio of reactant to silane	Reaction medium	Product	B.p. or m.p.,[a] °C.	Mm.	n^{20}D	Yield, %	Analyses Silicon, % Calcd.	Found
C_6H_5Li	4.6	Et_2O	$(C_6H_5)_4Si$[b]	M 234–235			40.5		
C_2H_5Li	8.6	Et_2O	$(C_2H_5)_4Si$[c]	B 149–150	737	1.4232	63.0		
C_2H_5Li	4.8	Pet. ether	$(C_2H_5)_3SiH$[d]	B 105–106	739	1.4112	36.0		
		(20–40°)	$(C_2H_5)_2SiH_2$[e]	B 53–56	739	1.3915	27.0		
i-C_3H_7Li	8.5	Pet. ether (20–40°)	$(i\text{-}C_3H_7)_3SiH$[f]	B 60	10	1.4365	37.5		
1-$C_{10}H_7Li$	14.5	Et_2O	$(1\text{-}C_{10}H_7)_3SiH$	M 236–237			39.0	6.81	6.64, 6.71
2-$C_{10}H_7Li$	2.7	Et_2O	$(2\text{-}C_{10}H_7)_4Si$[g]	M 216–217			50.0[k]		
C_6H_5Na	6.9	Et_2O	$(C_6H_5)_4Si$	M 234–235			21.0	8.33	8.24, 8.21
C_2H_5OH and C_2H_5OLi	37.0	C_2H_5OH	$(C_2H_5O)_4Si$[h]	B 167–168	740	1.3830	67.0		
n-C_3H_7OH and n-C_3H_7OLi	28.0	n-C_3H_7OH	$(n\text{-}C_3H_7O)_4Si$[i]	B 73.5	3	1.4020	77.5	10.62	10.60, 10.55
n-C_4H_9OH and n-C_4H_9OLi	26.0	n-C_4H_9OH	$(n\text{-}C_4H_9O)_4Si$[j]	B 138–140	11	1.4134	41.0	8.85	8.71, 8.71

[a] All melting points and boiling points are corrected. [b] S. Sugden and H. Wilkins, *J. Chem. Soc.*, 126 (1931), report the melting point as 234°. [c] M. Manulkin, *J. Gen. Chem., U. S. S. R.*, **16**, 235 (1936), reports the boiling point as 150–151° (760 mm.) and n^{20}D as 1.4234. [d] F. C. Whitmore, *et al.*, THIS JOURNAL, **69**, 2108 (1947), report the boiling point as 107° (733 mm.) and n^{20}D as 1.4117. [e] A. E. Finholt, *et al.*, *ibid.*, **69**, 2692 (1947), report the boiling point as 53–57° (760 mm.) and n^{20}D as 1.3918. [f] H. Gilman and R. N. Clark, *ibid.*, **69**, 1499 (1947), report the boiling point as 60–61° (3.5 mm.) and n^{20}D as 1.4358. [g] H. Gilman, *et al.*, *ibid.*, **72**, 4280 (1950), report the melting point as 216–217°. [h] H. D. Cogan, *et al.*, *Ind. Eng. Chem.*, **39**, 1364 (1947); L, Holzapfel, *et al.*, *Z. Elektrochem.*, **47**, 327 (1941), report the boiling point as 168.1° (760 mm.) and n^{20}D as 1.3832. [i] G. Abati, *Z. phys. Chem.*, **25**, 353 (1898), reports the boiling point as 225–227° (760 mm.). [j] D. Peppard, *et al.*, THIS JOURNAL, **68**, 77 (1946), report the boiling point as 140–142° (32 mm.) and n^{20}D as 1.4131. [k] This yield is based upon the quantity of 2-$C_{16}H_7Li$ used.

layer was extracted with a suitable solvent. The solvent was distilled from the organic layer and from the extract. Where solid products were obtained they were recrystallized and identified by their melting points and in certain cases by analysis. Liquid products were identified by means of boiling points and refractive indices as well as by analysis of certain samples. The results of these experiments are summarized in Table I.

Reaction of Silane with Alcohols.—For reaction of silane with alcohols it was found necessary to have present some alkoxide ions as catalysts. These were provided by adding one-half gram of metallic lithium to 100 ml. of alcohol. With the lower aliphatic alcohols lithium reacted very vigorously and gave clear solutions. With the higher alcohols the reaction with lithium was much less vigorous and required gentle heating to complete the reaction.

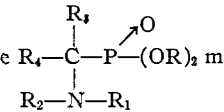
Following treatment of the alcohol containing alkoxide ions with silane for the proper length of time, the excess alcohol was removed by distillation (under vacuum in the case of the higher alcohols) and the products of the reaction were further purified by vacuum distillation. The results of these experiments are also included in Table I.

BLOOMINGTON, INDIANA

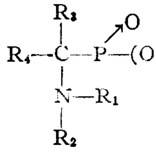
RECEIVED OCTOBER 15, 1951

The Synthesis of Esters of Substituted Amino Phosphonic Acids[1a]

BY ELLIS K. FIELDS[1b]

It has been found that compounds of structure  $\mathrm{R_4{-}\overset{\displaystyle R_3}{\underset{\displaystyle R_2{-}N{-}R_1}{C}}{-}\overset{\nearrow O}{P}{-}(OR)_2}$ may be synthesized by treating a phosphorus acid diester with (1) an aldehyde or ketone and an amine, (2) an α-alkylol amine, (3) an alkylidene diamine, (4) an N-disubstituted amino methyl ether, (5) an aldimine or ketimine derived from a primary amine. The various methods of preparation and some unusual properties of the new amino phosphonic esters are described.

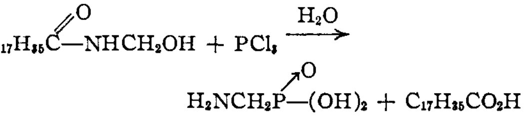
This paper is concerned with the synthesis of esters of N-substituted aminomethylphosphonic acids. These compounds have the structure



$$\mathrm{R_4{-}\overset{\displaystyle R_3}{\underset{\underset{\displaystyle R_2}{N{-}R_1}}{C}}{-}\overset{\nearrow O}{P}{-}(OR)_2}$$

where any of the R's may be hydrogen with the exception that R_1 and R_2 may not both be hydrogen.

The only method of synthesis of such compounds known heretofore consists of treating a methylol amide with phosphorus trichloride in the presence of acetic acid and hydrolyzing the product.[2]

(I) 

$$\mathrm{C_{17}H_{35}\overset{O}{\overset{/\!\!/}{C}}{-}NHCH_2OH + PCl_3 \xrightarrow{H_2O} H_2NCH_2\overset{\nearrow O}{P}{-}(OH)_2 + C_{17}H_{35}CO_2H}$$

This method has the following disadvantages: (1) it involves prolonged reaction times: from 12 hours to 7 days are necessary to complete the re-

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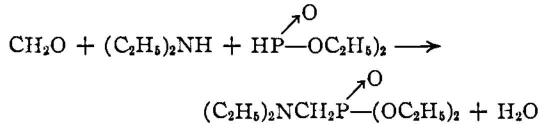
[1] (a) Presented at the XIIth International Congress of Pure and Applied Chemistry, New York, September, 1951; (b) present address: Standard Oil Company (Indiana), Whiting, Indiana.

[2] M. Engelmann and J. Pikl, U. S. Patent 2,304,156, December 8, 1942; U. S. Patent 2,304,157, December 8, 1942; Pikl, U. S. Patent 2,328,358, August 31, 1943.

action; (2) it is limited to the amino derivatives of methylphosphonic acid and cannot be used to prepare amino derivatives of, *e.g.*, propyl- or isopropylphosphonic acids; (3) dialkylamino methyl phosphonic acids cannot be made directly.

We have found that an aldehyde or ketone reacts with a mixture of a phosphite diester, such as diethyl phosphite, and a primary or secondary amine to give substituted aminomethylphosphonic esters. The reaction of formaldehyde with diethyl phosphite and diethylamine is

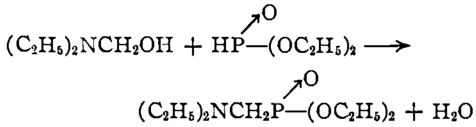
(II) 

$$CH_2O + (C_2H_5)_2NH + H\overset{\nearrow O}{P}{-}OC_2H_5)_2 \longrightarrow (C_2H_5)_2NCH_2\overset{\nearrow O}{P}{-}(OC_2H_5)_2 + H_2O$$

This reaction is exothermic and vigorous. The product in II, diethylaminomethylphosphonic acid diethyl ester, is obtained in 94% yield.

It is likely that diethylaminomethanol is formed first, and this reacts with diethyl phosphite to give the final product

(III) (1) $CH_2O + (C_2H_5)_2NH \longrightarrow (C_2H_5)_2NCH_2OH$

(2) 

$$(C_2H_5)_2NCH_2OH + H\overset{\nearrow O}{P}{-}(OC_2H_5)_2 \longrightarrow (C_2H_5)_2NCH_2\overset{\nearrow O}{P}{-}(OC_2H_5)_2 + H_2O$$

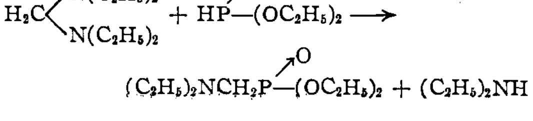
α-Alkylolamines have been prepared from various secondary amines and aldehydes. These, on treatment with diethyl phosphite, give the same products as are obtained from the aldehyde, amine and diethyl phosphite.

The alternative mechanism is the formation of α-hydroxymethyl phosphonic esters from the carbonyl compound and phosphite ester, followed by reaction with the amine to eliminate water and give the aminomethylphosphonic ester. This mechanism does not operate, since α-hydroxymethylphosphonic esters do not react with amines except at high temperatures.

The two methods of preparation of aminophosphoric esters illustrated in II and III are of general application. Unlike the Mannich reaction which they resemble they can be used with a wide variety of aldehydes and ketones and amines. The yields are usually over 70%. The products are quite pure even before distillation.

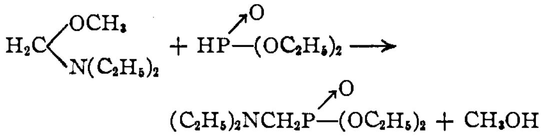
Water is formed as a product of these reactions. This is unimportant in most cases where the reaction is very rapid. When high-molecular weight reactants are used the rate of reaction may be slow enough for appreciable hydrolysis of the phosphite ester to occur.

The following two methods were found to give good yields of products and avoid the formation of water entirely: (1) The reaction of a tetrasubstituted alkylidene diamine with a dialkyl phosphite (Equation IV)

(IV) 

$$H_2C\begin{matrix}\nearrow N(C_2H_5)_2\\ \searrow N(C_2H_5)_2\end{matrix} + H\overset{\nearrow O}{P}{-}(OC_2H_5)_2 \longrightarrow (C_2H_5)_2NCH_2\overset{\nearrow O}{P}{-}(OC_2H_5)_2 + (C_2H_5)_2NH$$

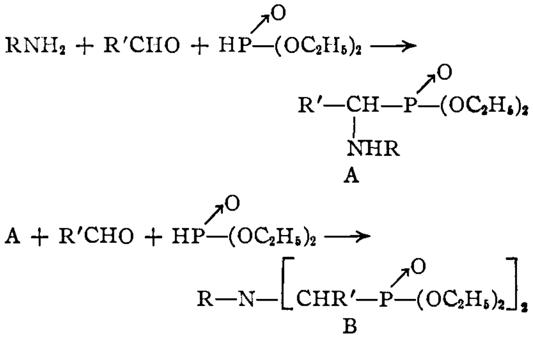
(2) The reaction of an α-dialkylamino methyl ether[3] with a dialkyl phosphite (Equation V)

(V) 

$$H_2C\begin{matrix}\nearrow OCH_3\\ \searrow N(C_2H_5)_2\end{matrix} + H\overset{\nearrow O}{P}{-}(OC_2H_5)_2 \longrightarrow (C_2H_5)_2NCH_2\overset{\nearrow O}{P}{-}(OC_2H_5)_2 + CH_3OH$$

The methods shown by equations IV and V give nearly quantitative yields of products.

Primary amines give much lower yields of pure products with aldehydes or ketones and phosphite diesters. This may be due to further reaction of the primary reaction product A (Equation VI)

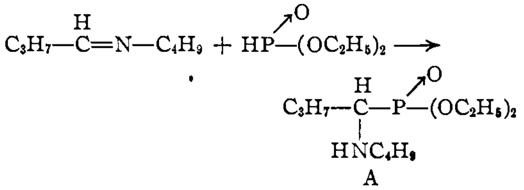
(VI) 

$$RNH_2 + R'CHO + H\overset{\nearrow O}{P}{-}(OC_2H_5)_2 \longrightarrow \underset{\text{A}}{R'{-}\underset{NHR}{\underset{|}{C}H}{-}\overset{\nearrow O}{P}{-}(OC_2H_5)_2}$$

$$A + R'CHO + H\overset{\nearrow O}{P}{-}(OC_2H_5)_2 \longrightarrow \underset{\text{B}}{R{-}N{-}\left[CHR'{-}\overset{\nearrow O}{P}{-}(OC_2H_5)_2\right]_2}$$

Considerable amounts of undistillable residues, probably of composition B, are obtained in this reaction.

It was discovered that imines react vigorously with phosphite diesters to give the secondary amine of type A (Equation VII)

(VII) 

$$C_3H_7{-}\overset{H}{C}{=}N{-}C_4H_9 + H\overset{\nearrow O}{P}{-}(OC_2H_5)_2 \longrightarrow \underset{\text{A}}{C_3H_7{-}\underset{HNC_4H_9}{\underset{|}{\overset{H}{C}}}{-}\overset{\nearrow O}{P}{-}(OC_2H_5)_2}$$

This reaction is general for aldehyde and ketone imines. Formaldimines polymerize too rapidly, but formaldimines derived from amino tertiary alkanes may be used. The ketone imines may be prepared in good yields by agitating a mixture of ketone and primary amine with anhydrous potassium carbonate. The reaction of the imine with a phosphite diester takes place simply by mixing equimolar quantities of the two reactants. The mixture becomes hot, usually after an induction period of several minutes. The yields of product are almost quantitative.

The substituted aminomethylphosphonic esters are colorless or light yellow mobile liquids which may be distilled *in vacuo*. The lower members are very soluble in water. Diethyl α-diethylaminomethylphosphonate resembles its carbon analog, ethyl N-diethylglycinate, in that it dissolves in cold water but separates out when the solution is heated.

The esters are soluble in all the common organic solvents. They are extremely stable to acids and bases, especially those esters derived from secondary amines. Diethyl α-diethylaminomethyl phos-

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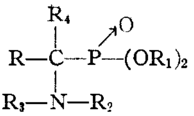
[3] C. M. McLeod and G. M. Robinson, *J. Chem. Soc.*, **119**, 1472 (1921).

TABLE I

ESTERS OF SUBSTITUTED AMINOMETHYLPHOSPHONIC ACIDS



$$R-\overset{R_4}{\underset{R_3-N-R_2}{C}}-\overset{\nearrow O}{P}-(OR_1)_2$$

Method of prepn.[c]	R	R₄	R₁	R₂	R₃	Yield, %	B.p., °C.	Mm.	Nitrogen, % Calcd.	Nitrogen, % Found	Phosphorus, % Calcd.	Phosphorus, % Found
A	H	H	Methyl	Methyl	Methyl	88	88	2	7.18	7.01	15.91	15.68
A, B	H	H	Ethyl	Ethyl	Ethyl	94	96	3	6.28	6.04	13.91	13.88
A, B	H	H	Ethyl	*i*-Propyl	*i*-Propyl	91	112	2	5.58	5.48	12.36	12.11
A, B	H	H	Ethyl	Butyl	Butyl	94	127	2	5.02	4.88	11.12	11.14
A	H	H	Ethyl	Cyclohexyl	Cyclohexyl	81	149	2	4.23	4.04	9.37	9.00
A	H	H	Ethyl	Octyl	Octyl	86	175	2	3.58	3.51	7.94	7.96
A	H	H	Ethyl	Oxybisethylene[a]		92	137	3	5.91	5.81	13.09	12.94
A	H	H	Ethyl	Pentamethylene[b]		87	124	3	5.96	5.71	13.20	13.08
A	H	H	Ethyl	Ethyl	Phenyl	47	126	1	5.17	4.93	11.45	11.37
A, C	H	H	Ethyl	H	Butyl	38, 89	114	2.5	6.28	6.18	13.91	13.84
A, C	H	H	Ethyl	H	*β*-Phenylethyl	32, 91	109	0.4	5.15	4.81	11.40	11.18
A	H	Methyl	Ethyl	Ethyl	Ethyl	81	94	1	5.91	5.78	13.09	13.01
A	H	Ethyl	Ethyl	Ethyl	Ethyl	78	95	0.8	5.58	5.56	12.36	12.48
A, B	H	Propyl	Ethyl	Ethyl	Ethyl	79	104–107	1	5.28	5.08	11.71	11.68
A	Me	Methyl	Ethyl	Ethyl	Ethyl	64	103–105	2–5	5.58	5.38	12.36	12.41
A	H	*α*-Furyl	Ethyl	Ethyl	Ethyl	84	140	2	4.84	4.81	10.73	10.81
A	H	Vinyl	Ethyl	Ethyl	Ethyl	87	116	4	5.69	5.64	12.61	12.60
A	H	Propyl	Ethyl	Butyl	Butyl	91	147	2	4.36	4.34	9.67	9.47
A	H	H	Butyl	Ethyl	Ethyl	93	131	1	5.03	5.01	11.12	10.98
A	H	H	2-Ethylhexyl	Ethyl	Ethyl	90	162–166	0.7	3.58	3.47	7.93	7.87
C	H	Methyl	Ethyl	H	Methyl	94	87	2.2	7.18	7.03	15.91	15.84
C	H	Methyl	Ethyl	H	Ethyl	91	84	1	6.70	6.71	14.84	14.88
C	Me	Methyl	Ethyl	H	Ethyl	97	91	2.3	6.28	6.04	13.91	13.65
C	H	Propyl	Ethyl	H	Methyl	93	110	1.5	6.28	6.18	13.91	13.84
C	H	Propyl	Ethyl	H	Butyl	94	119	2	5.28	5.19	11.70	11.66
C	H	Ethyl	Ethyl	H	Ethyl	89	93	1.5	6.28	6.21	13.91	13.81
C	H	Propyl	Butyl	H	Methyl	84	118–122	2	5.02	4.88	11.12	11.06
C	H	Phenyl	Ethyl	H	Phenyl	97	92 (m.p.)		4.39	4.40	9.73	9.68
C	H	*α*-Furyl	Ethyl	H	Ethyl	85	127	0.75	5.36	5.11	11.88	11.72
C	H	Phenyl	Ethyl	H	*p*-Methoxy phenyl	89	Sirup		4.18	4.39	9.26	9.01
C	H	Phenyl	Ethyl	H	Bis[d] ethylene	97	95 (m.p.)		5.47	5.41	12.12	12.03
C	H	Propyl	Ethyl	H	1-Diethyl amino-4-pentyl	84	133–135	2	8.91	9.27	10.41	10.16
C	H	*p*-Methoxy phenyl	Ethyl	H	1-Diethyl amino-4-pentyl	92	[e]		6.35	6.76	7.17	6.89
C	H	*o*-Chloro-phenyl	Ethyl,	H	Methyl	88	130–132	1.5	4.81	4.80	10.66	10.61
C	H	H	Ethyl	H	2,4,4-Trimethyl-2-pentyl	96	123	0.74	5.03	4.94	11.12	11.31

[a] From morpholine. [b] From piperidine. [c] See Experimental part. [d] From dibenzalethylenediamine. [e] Decomposed on attempted distillation.

phonate may be refluxed 48 hours with either concentrated hydrochloric acid or 10% aqueous sodium hydroxide without undergoing appreciable hydrolysis. Concentrated alcoholic potassium hydroxide or 48% aqueous hydrobromic acid hydrolyzes the esters on 1–5 hours heating to give acid or metal salts of the aminophosphonic acids. The alkali and alkaline earth salts of the lower aminophosphonic acids are water soluble.

The esters are also extremely resistant to the action of strong oxidizing agents. This caused some difficulty in the analysis for phosphorus. Samples had to be digested with perchloric acid and catalyst about five times as long as for other organic phosphorus compounds. Kjeldahl digestion gave very low values for nitrogen.

It was difficult to obtain the free aminophosphonic acids in pure form. Generally, noncrystallizing hygroscopic sirups resulted. In many cases the metal salts were also hygroscopic.

The new amino phosphonic esters are listed in Table I.

Experimental

General Procedure, A.—The aldehyde or ketone was added to a stirred mixture of equimolar quantities of secondary amine and phosphite diester at a rapid rate. The temperature was kept below 85°. Fifteen minutes after the addition was ended the mixture was cooled, dried over anhydrous sodium sulfate, filtered and distilled *in vacuo*.

If the order of addition were changed so that the amine was added to a mixture of phosphite diester and aldehyde, the product consisted of a mixture of compounds. This will be discussed in a subsequent article.

B.—An equimolar mixture of substituted methylenediamine or dialkylamino methyl ether with the phosphite diester was warmed to 60–95° in a flask connected to a take-off condenser. A vigorous reaction usually took place and secondary amine or alcohol, respectively, distilled. The reaction flask was heated to complete the distillation of liberated amine or alcohol, and finally the product was distilled *in vacuo*.

C.—The imines were prepared by treating the aldehyde or ketone with the primary amine in the presence of anhydrous potassium carbonate, separating the imine from the aqueous layer and drying thoroughly over potassium hydroxide. The imines of low molecular weight were distilled prior to use as they tended to polymerize, especially when not completely dried.

An equimolar mixture of imine and phosphite ester was allowed to stand until no more heat was evolved, then distilled *in vacuo*. Cooling was necessary when lower molecular weight imines were reacting.

Reaction of α-Alkylol Amines with Dialkyl Phosphites.—α-Hydroxymethyldiethylamine and α-hydroxymethyldiisopropylamine were prepared by the method of Henry[4] and

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(4) L. Henry, *Bull. soc. chim.*, [3] **13**, 158 (1895).

treated separately with equimolar quantities of diethyl phosphite. The ethyl esters of α-diethylaminomethyl- and α-diisopropylaminomethylphosphonic acids were obtained in almost quantitative yields.

Attempted Reaction of α-Hydroxymethylphosphonic Esters with Amines.—The ethyl ester of α-hydroxymethylphosphonic acid[5] was heated with diethylamine. There was no reaction at 56° after six hours or at 110° in a bomb after six hours. At 175° the mixture gave a dark resinous mass, in which the odor of phosphine was evident.

Preparation of Acetone-ethylimine.—A mixture of one mole of acetone, a 5% excess over one mole diethylamine and 10 g. of anhydrous potassium carbonate was refluxed for 30 minutes. The cooled organic layer was separated, dried over anhydrous potassium carbonate and filtered. It was not distilled, but used as such. The yield was about 80%.

Preparation of Phosphorous Acid Diesters.—Diethyl phosphite was purchased from Victor Chemical Company, Chicago, Illinois. The other phosphite esters were obtained by alcoholysis. A 10% excess over two moles of alcohol, one mole diethyl phosphite and 20% xylene based on the volume of diethyl phosphite was heated at 140° until 80–85% of the theoretical amount of ethanol had distilled. The reaction mixture was distilled *in vacuo*. The yields were about 85%. Esters of alcohols higher than 2-ethylhexanol would probably be difficult to distil without considerable decomposition.

Great care should be taken in the distillation of di-(2-chloroethyl) phosphite not to admit air until the distilling flask has cooled. At temperatures above 130° in air, decomposition occurs, phosphine is liberated and the entire mass ignites.

The phosphite esters used boiled as follows: di-*n*-amyl phosphite 107° at 1.4 mm.; di-2-ethylhexyl phosphite 145° at 1.3 mm.; di-(β-chloroethyl) phosphite 130° at 2.2 mm.

WHITING, INDIANA RECEIVED SEPTEMBER 21, 1951

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[5] The preparation and properties of esters of α-hydroxyalkyl phosphonic acids will be described in a forthcoming publication.

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

Electronic Chemical Potential in Chemisorption and Catalysis

BY M. BOUDART

The electronic chemical potential of a semi-conductor changes with temperature and impurity concentration. This variation is essential to the properties of semi-conducting surfaces in adsorption and catalysis. A qualitative discussion of induced heterogeneity and of its consequences may be given on the basis of a simple model of a catalyst surface. Active centers are still essential but their localized description becomes superfluous. A consequence of the dynamic picture of a catalytic surface presented here is the necessity of devising methods for characterizing the surface during the global catalytic reaction.

The role played by the electronic chemical potential of a clean metal in chemisorption, solubility of gases and catalysis has been recently emphasized by various investigators.[1–4] Fruitful correlations between heats of chemisorption or activation energies of certain catalytic reactions and the chemical potential of the metallic electrons or the Fermi level have thus been obtained. Since the Fermi level of a metal is practically independent of temperature but may be modified by alloying elements, a study of alloy catalysis seems quite appropriate, as was early recognized by Rienäcker.[5]

On the other hand, the literature on chemisorption and catalysis describes especially the behavior of non-metallic surfaces, "dirty" or "practical" catalysts. Among these must be included the so-called metallic catalysts which have not been prepared by special techniques (*e.g.*, evaporation), in order to obtain clean surfaces. Although such surfaces are not amenable to a quantitative theoretical analysis at the present time because of our ignorance of their surface energy levels, it seems worthwhile nevertheless to examine how the variation of the electronic chemical potential in non-metallic solids may affect adsorptive and catalytic properties.

(1) The Nature of an Adsorbent Surface.—It will be assumed that a non-metallic adsorbent surface may be treated as a two-dimensional semi-conductor system. Qualitatively, the well-known results of semi-conductor theory, as applied to three-dimensional crystals, may be applied to our model of an adsorbent surface. From a quantitative point of view, the following particularities must be pointed out: (1) the distribution of energy levels at the surface is different from the one prevailing in the bulk of the crystal. (2) Departure from stoichiometry on the surface is not limited to low values, as is usual in the bulk material owing to structural limitations. Similarly, impurities may be present at the surface in concentrations substantially larger than would be tolerated by the three-dimensional lattice without phase separation. (3) Impurity levels in the two-dimensional matrix have a threefold origin (a) deviations from stoichiometry, (b) foreign admixtures introduced into the adsorbent matrix during its preparation, (c) the adsorbed species. Vol'kenshtein[6,7] has emphasized the necessity of including the impurity levels due to chemisorbed atoms or molecules. (4) The results of semi-conductor theory which will be required do not depend on the validity of the band description of ionic solids. They may be derived from straightforward thermodynamical arguments, as developed by Wagner and Schottky.[8] Applicability of Maxwell–Boltzmann statistics is all that is required. Nevertheless, for the sake of clarity, the usual band representation will be used, in conformity with general practice. For instance, Wright and Andrews[9] successfully interpret their data obtained with NiO on the basis of a

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