$HNR_2 \geqslant NR_3$. For amines with more bulky alkyl groups (propyl and butyl), the maximum of steric strain occurs with the secondary amines and thereafter the $-\Delta H$ values do not decrease. This series of the bond strength is equal to that of acid-base equilibria of methylamines in aqueous solution.[14]

It is interesting to compare the $-\Delta F$ and $-\Delta H$ values for the homologous series methylamine, ethylamine, *i*-propylamine, *t*-butylamine which is derived from the successive substitution of a C–H hydrogen atom by a methyl group in methylamine. The values of $-\Delta F$ and $-\Delta H$ plotted against $-\Sigma\sigma^*$ show a maximum at *i*-propylamine. The sequence of increasing affinity $(-\Delta F)$ and bond strength $(-\Delta H)$ are

$$H_2NCH_3 < H_2NCH_2CH_3 < H_2NCH(CH_3)_2 > H_2NC(CH_3)_3$$

Here, too, there are opposing polar and steric factors. Beyond *i*-propylamine the steric effect predominates and the values of $-\Delta F$ and $-\Delta H$ decrease. Stuart models show that the bulky $C(CH_3)_3$ group prevents the nitrogen atom from sufficiently approaching the nickel atom in a direction suitable for the formation of a tetrahedral bond with respect to the nitrogen atom.

The free energy data reported here and those found for the equilibria with H^+ in water and the acceptors BEt_3 and $B(t\text{-}Bu)_3$ in the gas phase[15] permit a comparison of the relative donor properties of the alkylamines toward the different acceptors.

These results also give some information on the steric requirements of the different acceptors. The diagram in Fig. 3 shows that the steric requirements of NiDBH are intermediate between those of BEt_3 and $B(t\text{-}Bu)_3$, the series of increasing steric requirements for different acceptor being: $H^+ < BMe_3 <$ NiDBH $< B(t\text{-}Bu)_3$. Since the four coordinated atoms and the nickel in the NiDBH are coplanar, this suggests that the hydrogen atoms of the *tert*-butyl groups in $B(t\text{-}Bu)_3$ extend beyond the plane which contain the boron atom.[16]

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(14) D. H. Everett and W. F. K. Wynne-Jones, *Trans. Faraday Soc.*, **35**, 1380 (1939).

(15) H. C. Brown, *J. Chem. Soc.*, 1248 (1956), and references quoted therein.

(16) It should be pointed out that the acceptor reported as $B(t\text{-}Bu)_3$ was in fact triisobutylboron (*cf.* G. F. Hennion, P. A. McCusker, E. C. Ashby and A. J. Rutkowski, This Journal, **79**, 5190 (1957). However this in no way may change the discussion presented here.

[Contribution from the Department of Chemistry, University of Wisconsin, Madison, Wisconsin]

Hydrogen Bonding Studies.[1a] IV. Acidity and Basicity of Triphenylhydroxy Compounds of the Group IVB Elements and the Question of Pi-bonding from Oxygen to Metals[1b]

By Robert West, Ronald H. Baney and David L. Powell

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The acidity[2] and basicity[2] as hydrogen bond donors and acceptors have been measured for the compounds Ph_3MOH, where M = C, Si, Ge, Sn and Pb. The trends in acidity and basicity in these compounds indicate that dative pi-bonding from oxygen to M is strong in Ph_3SiOH, weaker in Ph_3GeOH, and negligible in the other three compounds.

Dative pi-bonding to silicon is now fairly well established as a fact of organosilicon chemistry,[3] but the possibility of pi-bonding to the other group IVB metals has received less attention. The two previous comparative studies of pi-bonding to group IV metals deal with pi-bonding from aromatic rings to these elements. Chatt and Williams have measured the dissociation constants of aromatic acids substituted in the para position by a carbon, silicon, germanium or tin trialkyl group,[4] while Benkeser, DeBoer, Robinson and Sauve have determined the Hammett sigma constants for *para* triphenysilyl and triphenylgermanyl groups by reaction rate studies.[5a] Chatt and Williams found that *pK* values for the Si, Ge and Sn compounds were all slightly greater than for the carbon compound but differed little among themselves.[4] They explained these findings on the basis that dative pi-bonding from the aromatic ring to the metal atom takes place to about the same extent in the Si, Ge and Sn compounds. In agreement with this interpretation Benkeser concluded that the amount of pi-bonding to germanium and silicon is essentially identical.[5a] In the one theoretical paper which has appeared on the subject of $p\pi$–$d\pi$ bonding, the prediction is made that the strength of this type of bonding should not be strongly dependent upon the radius of the atom bearing the d-orbitals

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(1) (a) Previous paper in this series: G. Hite, E. E. Smissman and R. West, This Journal, **82**, 1207 (1960). (b) This research was supported by the United States Air Force through the Air Force Office of Scientific Research of the Air Research and Development Command, under Contract No. AF 49(638)-285. Reproduction in whole or part is permitted for any purpose of the United States Government.

(2) Henceforth, in this and succeeding papers in this series, unless otherwise specified the terms "acidity" and "basicity" will refer to Lewis acidity and Lewis basicity in hydrogen bonding reactions; that is, to relative proton donating power and proton attracting power, respectively, in hydrogen bond formation. This terminology may be questioned on the basis that the hydrogen bonding interaction is different from other types of Lewis acid-base interaction. This point is debatable, but the authors feel that the similarity between hydrogen bonding and other Lewis-acid-base reactions is great and that at present it is preferable to consider hydrogen bonding in terms of Lewis acid-base theory; *cf.* the terminology used in G. C. Pimentel and A. L. McClellan, "The Hydrogen Bond," Freeman and Co., San Francisco, 1960.

(3) F. G. A. Stone and D. Seyferth, *J. Inorg. Nuclear Chem.*, **1**, 112 (1955).

(4) J. Chatt and A. A. Williams, *J. Chem. Soc.*, 4403 (1954).

(5) (a) R. A. Benkeser, C. E. DeBoer, R. E. Robinson and D. M. Sauve, This Journal, **78**, 682 (1956); (b) D. P. Craig, A. Maccoll, R. S. Nyholm, L. E. Orgel and L. E. Sutton, *J. Chem. Soc.*, 332, 354 (1954).

and might even become stronger with increasing radius of that atom.[5b]

In this paper, we are reporting the results of a comparative study of pi-bonding from oxygen to the elements of group IVB. We have investigated the acidity and basicity of some organohydroxy compounds of the IVB group elements as hydrogen bond donors and acceptors. The triphenylhydroxy compounds were chosen as a matter of convenience since the complete isostructural series was available by known preparative methods. Both the proton donating power (acidity)[2] and the proton accepting power (basicity)[2] of hydroxyl compounds can be studied by means of infrared spectroscopy, as Kuhn showed in 1952.[6] Relative acidities can be studied by measuring the frequency shift of the hydroxyl stretching absorptions upon hydrogen bonding to a reference base. Relative basicities similarly can be measured by admixture of the hydroxyl compounds with a more powerful proton donor and measurement of the shift of the hydrogenic stretching frequency of the proton donor. In our work, phenol was used as the proton donor and ether as the reference base.

In an investigation reported recently,[7] we employed these techniques to determine the relative acidity and basicity of a number of silanols and carbinols. Silanols were found to be much more acidic, but only slightly less basic, than analogous carbinols. These results were taken to indicate that dative pi-bonding from oxygen to silicon occurs in silanols, involving only one of the two unshared electron pairs on oxygen.[8]

Experimental

Materials.—Triphenylcarbinol prepared from benzophenone and phenylmagnesium bromide was recrystallized twice from benzene–petroleum ether and twice from ethanol, m.p. 159–160°. Triphenylsilanol was prepared by the alkaline hydrolysis of purified triphenylchlorosilane[9] and recrystallized from benzene, m.p. 153–154°, lit. 155°.[10] Eq. wt: calcd. 276, found 273.[11] Merck reagent grade carbon tetrachloride from freshly-opened bottles was used as solvent; the infrared absorption due to water content was negligible. The phenol was reagent grade material purified by fractional crystallization and fractional distillation. Mallinckrodt anhydrous ether was used as received.

Triphenylgermanol.—Triphenylbromogermane was prepared from tetraphenylgermane by treatment with bromine.[12] Basic aqueous hydrolysis of this material is reported to give only hexaphenyldigermoxane.[13] We obtained triphenylgermanol by treatment of Ph_3GeBr with alcoholic potassium hydroxide, as recommended by Brook and Gilman.[14] After recrystallization from chloroform–petroleum ether, the product had m.p. 133–134°, lit. 134.2°.[13]

Triphenyllead Hydroxide.—Triphenyllead chloride, kindly furnished by H. G. Petrie of the Ethyl Corporation, Baton Rouge, La., was converted to the hydroxide by basic hydrolysis. In 40 ml. of ethanol was dissolved 1.89 g. (0.004 mole) of Ph_3PbCl. To this solution was added 0.4 g. of potassium hydroxide dissolved in 4 ml. of water. The mixture was refluxed for 3 hr., filtered while hot and then cooled. The white crystalline product crystallized and was filtered off; yield 1.80 g., 100%. The compound decomposed without melting at 300–310°.

Anal. Calcd. for $C_{18}H_{16}OPb$: C, 47.49; H, 3.52. Found: C, 47.31; H, 3.43.

Triphenyltin Hydroxide.—Commercial samples of this material from the Metal and Thermit Co. and from Anderson Laboratories were found to be grossly contaminated with tetraphenyltin and diphenyltin oxide. However, the commercial hydroxide could be purified by extraction with ethanol and conversion to triphenyltin chloride. To effect purification, the commercial hydroxide was first taken up in ethanol, leaving most of the impurities behind as an insoluble residue. The ethanol was evaporated and the crude hydroxide was converted to triphenyltin chloride by grinding in a mortar under 12 *N* hydrochloric acid. The acid solution was evaporated to give triphenyltin chloride. A sample of the crude chloride recrystallized from ethanol had m.p. 104–105°, lit.[15] 105–106°.

Alkaline hydrolysis of triphenyltin chloride then yielded the desired triphenyltin hydroxide. The chloride was taken up in diethyl ether and stirred with excess aqueous ammonia. The ether layer was separated and dried and triphenyltin hydroxide was obtained by evaporation of the ether layer, recrystallization from ethanol and drying *in vacuo*. The white crystals melted at 119–120°, with some cloudiness remaining in the melt above 120°.

Anal. Calcd. for $C_{18}H_{16}OSn$: C, 58.96; H, 4.40. Found: a: C, 58.04; H, 4.62; b: C, 59.27; H, 4.61; c: C, 59.55; H, 4.53.

In many repetitions of this and other methods for preparing triphenyltin hydroxide, even with careful and prolonged drying, we were unable to obtain a sample whose carbon tetrachloride solution did not show a water band in the infrared spectrum at 3681 cm.$^{-1}$. The presence of additional water also could be shown by titration with Karl Fischer reagent.[16] Analytical results for different samples varied, and some had carbon, hydrogen and "OH" percentages approaching the theoretical for Ph_3SnOH. However, even these samples contained water as shown by their infrared spectra. In these samples we believe that partial dehydration to triphenyltin oxide had taken place

$$2\ Ph_3SnOH \longrightarrow Ph_3SnOSnPh_3 + H_2O$$

Loss of water from this condensation reaction would compensate for the additional water present.

It is evident that Ph_3SnOH holds water tenaciously, as originally reported by Aronheim,[17] although later workers make no mention of this phenomenon.[18] The samples used in our infrared work contained from 0.1 to 0.5 mole of water per mole of Ph_3SnOH. Interpretation of the spectrum is complicated somewhat by the presence of water. Since water is more acidic than Ph_3SnOH, an association band appears in the mixture with ether, but the Sn–O–H band remains unchanged.

Spectra.—A Cary Model S spectrophotometer with quartz optics was used for measurements in the region of the first overtone of the O–H stretching absorption band. The integrated intensity of this band was measured for the compounds at concentrations of 0.01 *M* and below using the approximate method described by Tsubomura.[19] The extent of intermolecular association was determined from the absorbancy of this first overtone band at 0.08 *M*, compared with the absorbancy at infinite dilution, as described in our earlier paper.[7]

The equilibrium constants for association to tetrahydrofuran were also determined using the first overtone of the free O–H band. The 10 cm. cells were thermostatted at 25°. The intensity of the peak was taken as a measure of the concentration of unassociated molecules, and the remaining hydroxyl compound in solution was assumed to be present as a 1:1 complex with tetrahydrofuran.[20] Initial formal

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(6) L. P. Kuhn, THIS JOURNAL, **74**, 2492 (1952).

(7) R. West and R. H. Baney, *ibid.*, **81**, 6145 (1959).

(8) *Cf.* R. H. Baney, K. J. Lake, R. West and L. S. Whatley, *Chem. and Ind.* (*London*), 1129 (1959).

(9) A. Polis, *Ber.*, **19**, 1012 (1886).

(10) E. G. Rochow, "Introduction to the Chemistry of the Silicones," 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1951, p. 182.

(11) By titration with tetrabutylammonium hydroxide in pyridine; R. West and R. H. Baney, *J. Inorg. Nuclear Chem.*, **7**, 297 (1958).

(12) D. M. Harris, W. H. Nebergall and O. H. Johnson, *Inorg. Syntheses*, **5**, 70 (1957).

(13) C. A. Kraus and L. S. Foster, THIS JOURNAL, **49**, 457 (1927).

(14) A. G. Brook and H. Gilman, *ibid.*, **76**, 77 (1954).

(15) K. A. Kocheshkov, M. M. Nad and A. P. Alexandrov, *Ber.*, **67**, 1348 (1934).

(16) H. Gilman and L. S. Miller, THIS JOURNAL, **73**, 2367 (1951).

(17) B. Aronheim, *Ann.*, **194**, 174 (1878).

(18) E. Krause and R. Pohland, *Ber.*, **57**, 540 (1924); *cf.* ref. 16.

(19) H. Tsubomura, *J. Phys. Chem.*, **24**, 927 (1956).

(20) The intensity of the free OH peak was corrected for dimer formation, which was less than 4% in all cases. Details of the meas-

TABLE I

HYDROGEN BONDING PROPERTIES OF TRIPHENYLHYDROXY COMPOUNDS[a]

	ν_{OH}	$\Delta\nu_{PhOH}$	$\Delta\nu_{Et_2O}$	$\Delta\nu_{THF}$	K_{THF}	% assoc. 0.08 *M*	$\int A$
Ph_3COH	3609	172	174	208	0.90 ± 0.04	1	0.90 ± 0.03
Ph_3SiOH	3677	175	316	338	4.0 ± .2	19	1.27 ± .03
Ph_3GeOH	3651	288	198	211	0.84 ± .06	26	1.13 ± .03
Ph_3SnOH	3647	470	<10				0.33 ± .10
Ph_3PbOH	3618	Reacts	26				

[a] The column headed ν_{OH} gives the frequency of the free OH band in cm.$^{-1}$, ±2 cm.$^{-1}$; $\Delta\nu_{PhOH}$ gives the frequency shift of the phenol O–H band upon hydrogen bonding to the hydroxyl compound, ±10 cm.$^{-1}$; $\Delta\nu_{Et_2O}$ and $\Delta\nu_{THF}$ give the shift of the free OH band upon hydrogen bonding to ether and tetrahydrofuran, ±10 cm.$^{-1}$; K_{THF} gives the equilibrium constant for hydrogen bonding to tetrahydrofuran; $\int A$ gives the integrated absorbance of the first overtone of the free OH band.

concentrations of hydroxyl compounds, determined to three significant figures, were near 0.007 *M* for Ph_3GeOH, 0.01 *M* for Ph_3COH, and 0.02 *M* for Ph_3SiOH. Four runs were made for each hydroxyl compound at THF concentrations from 1.23 to 0.123 *M*. Equilibrium constants obtained were: Ph_3COH, 0.90, 0.91, 0.88, 0.90; Ph_3SiOH, 4.1, 4.1, 3.8, 4.1; Ph_3GeOH, 0.86, 0.85, 0.81, 0.86.

Other spectral measurements were carried out in the fundamental region using a Perkin-Elmer Model 112 spectrometer with a lithium fluoride prism, calibrated against water vapor and ammonia. Band positions were reproducible within ± 1 cm.$^{-1}$, and assignments are believed accurate to within ± 2 cm.$^{-1}$ for sharp bands. Broad association peaks, however, could be placed less precisely (Table I). Hydroxyl compounds ordinarily were present at 0.01 *M* in the mixtures with phenol and ether in carbon tetrachloride solvent. At this concentration absorption due to self-association was negligible. Saturated solutions of Ph_3SnOH and Ph_3PbOH were used. These were found to be 0.08 *M* and about 0.001 *M*, respectively. In mixtures with hydroxyl compounds, phenol was present at 0.01 *M* and ether at 0.25 *M*. A path length of 1 cm. was used for the band shift experiments, and a shorter path length of 3 mm. was used ordinarily for determining the position of the free OH bands.

When Ph_3PbOH was mixed with phenol, an immediate reaction took place. The phenol OH peak decreased markedly in intensity and a strong water band appeared at 3861 cm.$^{-1}$. The Ph_3PbOH hydroxyl absorption is partly masked by the phenol band, but it appeared to decrease also. This spectral evidence suggests that a neutralization reaction took place in the solution

$$Ph_3PbOH + C_6H_5OH \longrightarrow Ph_3PbOC_6H_5 + H_2O$$

Results and Discussion

Acidity and Basicity.—The basicity of the triphenyl hydroxy compounds, as shown by the phenol O–H frequency shifts (Table I), increases in the order $C \sim Si < Ge < Sn$. The hydrogen bonding basicity of triphenyllead hydroxide could not be studied because it underwent a rapid reaction with phenol, apparently forming triphenyllead phenoxide and water. However, the occurrence of this reaction, which amounts to a neutralization, indicates that the Brönsted basicity of the lead compound is very high.

The O–H frequency shifts shown by the compounds upon hydrogen bonding to ether and tetrahydrofuran increase in the order $Sn \sim Pb < C \sim Ge < Si$ (Table I). These $\Delta\nu$ values can be taken as a rough indication of the relative acidities. An exact correlation is not expected since the Badger–Bauer rule[21] relating $\Delta\nu$ with ΔH for hydrogen bonding cannot be expected to hold perfectly for hydroxyl groups in such different compounds. However, frequency shifts shown by the tin and lead compounds are relatively so small that it seems proper to conclude that these compounds are weaker acids than any of the others. It also seems clear from the $\Delta\nu_{OH}$ values that Ph_3SiOH is a stronger acid than any of the other compounds in the series.

The large value of the equilibrium constant for the association of triphenylsilanol to tetrahydrofuran provides additional evidence for the enhanced acidity of triphenylsilanol as a proton donor in hydrogen bonding. The protonic nature of the hydroxyl hydrogen in Ph_3SiOH is reflected in the fact that this compound can be titrated easily as an acid in pyridine,[11] while the germanium and carbon analogs are too weak as Brønsted acids to be titrated in this solvent. Ph_3COH and Ph_3GeOH give roughly equal frequency shifts upon hydrogen bonding to ethers and have nearly equal equilibrium constants for association to THF. Apparently the carbon and germanium compounds have similar strength as hydrogen bonding acids.

The intensities of the first overtone O–H stretching bands increase in the order $Sn < C < Ge < Si$ and so correlate well with the order of increasing acidity established above. The extent of intermolecular association at 0.08 *M* increases in the order $Ph_3COH < Ph_3SiOH < Ph_3GeOH$. Steric factors probably control the degree of polymerization by hydrogen bonding in solutions of these compounds.

Conclusions: Pi-bonding to Group IV Metals.—Dative pi-bonding from oxygen to the central atom cannot take place in Ph_3COH since carbon has no low-energy orbitals to overlap with *p* orbitals of oxygen. However, the possibility of dative pi-bonding must be considered in all the other compounds of the series. In the absence of pi-bonding, the basicity would be expected to decrease and the acidity to increase as the central atom becomes more electronegative, because of inductive effects. In particular, Ph_3SiOH would be expected to be more basic and less acidic than Ph_3COH or Ph_3GeOH, since silicon is now known to be less electronegative than either germanium or carbon.[22]

The enhanced acidity of Ph_3SiOH can be explained on the basis of strong dative pi-bonding in this compound, as discussed in our previous papers.[7,8] The basicity of the oxygen in Ph_3SiOH must be reduced considerably by pi-bonding, since Ph_3SiOH is much less basic than Ph_3GeOH. Our previous conclusion, that pi-bonding does not

urements and calculations will be published in the Ph.D. thesis of D. L. Powell, University of Wisconsin.

[21] R. M. Badger and S. H. Bauer, *J. Chem. Phys.*, **5**, 839 (1937); R. M. Badger, *ibid.*, **8**, 288 (1940).

[22] A. L. Allred and E. G. Rochow, *J. Inorg. Nuclear Chem.*, **5**, 269 (1958): C, 2.60; Si, 1.90; Ge, 2.00; Sn, 1.93; Pb, 2.45; A. L. Allred and E. G. Rochow, *ibid.*, **5**, 264 (1958): C, 2.50; Si, 1.74; Ge, 2.02; Sn, 1.72; M. A. Fineman and R. Daignault, *ibid.*, **10**, 205 (1959); *cf.* H. O. Pritchard and H. A. Skinner, *Chem. Revs.*, **55**, 745 (1955); R. T. Sanderson, THIS JOURNAL, **74**, 4792 (1952).

greatly influence the basicity of silanol oxygen,[7,8] must be modified accordingly.

Our data also indicate that pi-bonding is much stronger in Ph_3SiOH than in Ph_3GeOH. On the basis of inductive effects alone, Ph_3GeOH would be expected to be a stronger acid and a weaker base than Ph_3SiOH, while in fact the reverse is true. The high basicity of Ph_3GeOH can be attributed to the inductive effect of the germanium atom, which becomes apparent with weaker pi bonding in this compound.

Weak dative pi-bonding from oxygen to germanium probably does take place in Ph_3GeOH. The acidity of PhGeOH is approximately as great as that of Ph_3COH, while on the basis of inductive effects alone it should be much less. However, the data for Ph_3SnOH and Ph_3PbOH provide no indication of significant pi-bonding in these compounds.

Our conclusion is that in this series of compounds pi-bonding from oxygen to metal decreases markedly going from Si to Ge to Sn (and Pb).[23] This is in contrast to the theoretical predictions of Craig,[5b] as well as to the findings of Chatt and Williams[4] and of Benkeser,[5a] that the pi-bonding from aromatic rings to these metals takes place to about the same extent. Of course, dative pi-bonding from aromatic rings need not follow the same trend as pi-bonding from oxygen. The pi-electron cloud in the aromatic ring is perhaps more diffuse than the *p*-electron pairs on oxygen and hence may overlap better with the correspondingly diffuse d orbitals on the larger metal atoms.

Since our compounds were triphenyl derivatives, any dative pi-bonding from the aromatic rings which took place would compete with pi-bonding from oxygen. However, aromatic ring pi-bonding appears to be unimportant, in this series of compounds, compared to oxygen pi-bonding. Previously we have shown that trimethyl- and triethylsilanol are weaker acids and stronger bases than triphenylsilanol.[7] Hence the net effect of the aromatic rings is electron-withdrawing; the opposite would be true if aromatic ring pi-bonding were important. Similarly, the chemical evidence suggests that trialkyltin hydroxides are more basic and less acidic than triphenyltin hydroxide.[24] The question of competitive pi-bonding between oxygen and aromatic rings will be considered in more detail in another publication.

(23) *Cf.* R. West and R. H. Baney, *J. Phys. Chem.*, **64**, 822 (1960).

(24) J. G. A. Luitjen and G. J. M. Van der Kerk, "Investigations in the Field of Organotin Chemistry," Tin Research Institute, Middlesex, England, 1955.

[Contribution from the Department of Chemistry, Northwestern University, Evanston, Illinois]

Reactions between Hydrocarbons and Deuterium on Chromium Oxide Gel. I. General[1]

By Robert L. Burwell, Jr.,[2] A. B. Littlewood, M. Cardew, G. Pass and C. T. H. Stoddart

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Sites for hydrogenation of olefins and for isotopic exchange between alkanes and deuterium are simultaneously developed by heating chromium oxide gel to higher temperatures. Above 470°, the rate of loss of surface exceeds the rate of site production. There is little interaction among sites. Chromium oxide gel also catalyses double bond migration but on sites which, at least in part, differ from those involved in hydrogenation and exchange. The major processes, simple isotopic exchange of one atom per adsorption step and simple *cis*-addition of deuterium atoms to the double bond, involve a monoadsorbed alkane which cannot revert to a diadsorbed alkane at temperatures below 300°. It seems probable that olefin reacts with a surface hydrogen atom to form monoadsorbed alkane without proceeding through diadsorbed alkane. The preference for exchange of primary hydrogen atoms and the relative rates of exchange of a series of hydrocarbons suggest that the transition state separating alkane and monoadsorbed alkane involves some small contribution from carbanion. The very rapid exchange of cyclopropane probably results not only from this but also from isovalent hyperconjugation with surface sites in which a d-p π-bond is involved. The minor processes, multiple deuteration in isotopic exchange and the spreading of isotopic distribution patterns in the addition of deuterium to olefin, cannot, in general, involve gas phase olefin as an intermediate. Because of the absence of the minor processes in ethane exchange and in the deuterogenation of ethylene, it seems probable that an adsorbed allylic species is the intermediate.

During recent decades, it has become possible to analyze the mechanisms of a large number of organic reactions in terms of a reasonably restricted group of elementary reactions. Tentative approaches to a similar development are evident in heterogeneous catalysis and particularly in reactions between hydrocarbons and hydrogen on metallic catalysts. However, since characterization of elementary reactions between hydrocarbons and hydrogen solely on the basis of experiments on metallic catalysts might be seriously misleading, it seemed desirable to secure appropriate information on quite different catalysts. Accordingly, we have investigated a series of reactions on chromium oxide gel, chosen from the various catalysts of the oxide type because of its stability and because of the considerable information which has been accumulated about its catalytic and physical properties.

Paper I of this series will discuss our results and consider their mechanistic implications. Papers II–V will report the details of the isotopic exchange experiments, of the addition of deuterium to olefins and of the stereochemistry of these reactions.

The original work of Lazier and Vaughen[3]

(1) Some of the material has been the subject of a preliminary communication, R. L. Burwell, Jr., and A. B. Littlewood, This Journal, **78**, 4170 (1956), and also, Miami Meeting, American Chemical Society, April, 1957. General surveys have been presented at the Gordon Research Conference on Catalysis, 1959, and at the Conference on Organic Catalysis, Moscow, November 16, 1959.

(2) To whom inquiries concerning these papers should be directed.

(3) W. A. Lazier and J. V. Vaughen, This Journal, **54**, 3080 (1932).