

50-50 ASA-SAA. Subalpha: no m.p.; L.S. 37.1; S.S. 4.21(S), 3.79(M). Alpha: 31.9°; L.S. 36.8; S.S. 4.15(S).  
 50-50 APA-PAA. Subalpha: no m.p.; L.S. 34.2; S.S. 4.19(S), 3.90(M). Alpha: 18.9°; L.S. 33.7; S.S. 4.13(S).

### Results and Discussion

The alpha m.p.'s (rapid complete m.p.) of mixtures lie on straight lines connecting the m.p.'s of the components. By storage, the components were transformed to the stable form as was the 20% unsymmetrical mix of APA-PAA. In all other mixtures, storage for 2 months effected no transformation. There is a possibility that the alpha form is actually thermodynamically stable in some range of composition. Such true alpha stability would occur if the (unrealized) equilibrium curves, dropping from the stable-form m.p.'s of the components, fall sufficiently steeply on addition of second component to intersect the nearly linear alpha m.p. curve before they intersect each other.

In any case, in the region of  $\frac{2}{3}$  unsymmetrical isomer, which is the proportion to be expected from the interesterification method of preparing satu-

rated diacetins,<sup>2</sup> it is expected that the waxy alpha form would remain indefinitely stable.

It is a matter of interest that the m.p.'s of symmetrical are lower than those of unsymmetrical isomers as is the case with monoglycerides but not with di- and more familiar triglycerides.

The diffraction data for subalpha and alpha forms of the 50/50 mixes, both short and long spacings, are close to and for the most part intermediate between those of the components. It is of interest to note again slightly shorter long spacings for alpha than subalpha. The fact that the short spacings of the subalpha form of the palmitoyl mixture are nearer together at 0° than those of the stearyl mixture suggests a closer approach to the alpha configuration as is reasonable to expect for the lower melting palmitoyl mixture.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA, LOS ANGELES]

## The Ultraviolet Absorption Spectra of Aromatic Compounds Adsorbed on Silicic Acid

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Ultraviolet absorption spectra of mono- and di-substituted benzene derivatives adsorbed on activated silicic acid have been measured by suspending the silicic acid in an inert liquid of the same refractive index and recording the transmission spectrum of a 0.3-cm. layer of the slurry. The spectra are interpreted in terms of the effect of the interactions between the adsorbent and the adsorbate on the electronic states of the adsorbate.

The light absorbing properties of many compounds frequently change markedly when the compounds pass from the unadsorbed to the adsorbed state. Thus, for example, when a pale yellow compound such as *N,N*-diethyl-4-nitroaniline is adsorbed onto silicic acid from a non-polar solvent it often acquires a golden yellow color, and a compound which is normally yellow-orange may appear orange-red when adsorbed. These color changes result from perturbations of the electronic states of the molecule upon adsorption. Measurements of absorption spectra of molecules in the adsorbed state thus can provide information which in favorable circumstances may permit estimation of the extent of the electronic perturbation on adsorption and determination of the nature of the electronic states involved in the transition, and may also provide clues about the orientation of the molecule on the surface and the nature of the adsorption forces.

A simple and practical method for studying the spectra of compounds adsorbed on silicic acid was first suggested by an observation made by Trappe,<sup>2</sup> who reported that a column of silicic acid became transparent when it was wet with chloroform and no pressure was applied. The close similarity in the refractive indices of chloroform (1.446) and silicic acid (*ca.* 1.420) resulted in a minimum of

light scattering and refraction arising from optical inhomogeneities in the slurry. Slurries made from silicic acid and cyclohexane, which has a refractive index (1.426) closer to that of silicic acid than does chloroform, are sufficiently transparent in 0.3 cm. layers for spectrophotometric measurements at wave lengths above about 235  $m\mu$ . The lower limit on the wave length region available for investigation in the cyclohexane-silicic acid system is set by the divergence of the refractive indices for these two compounds in this region. Their refractive dispersions are sufficiently different that the transparency of the slurries decreases sharply at wave lengths below 260  $m\mu$ .<sup>3</sup>

The unhindered acidic proton of the silanol group of silicic acid appears to be ideal for hydrogen bonding and, in fact, the compounds most strongly adsorbed are those which are capable of acting as proton acceptors in hydrogen bonds.<sup>4</sup> In all of the adsorbent-adsorbate complexes studied here, except those formed by silicic acid with neutral compounds such as benzene and triphenylamine, it is believed that the silicic acid is acting as a proton donor in a hydrogen bond to some center of high electron density in the adsorbed molecule.

(3) This is essentially the well-known Christiansen-filter effect; see, *e.g.*, W. C. Price and K. S. Tetlow, *J. Chem. Phys.*, **16**, 1157 (1948).

(4) R. K. Iler, "The Colloid Chemistry of Silica and Silicates," Cornell University Press, Ithaca, N. Y., 1955, p. 59.

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(2) W. Trappe, *Biochem. Z.*, **305**, 150 (1940).

There have been several pertinent earlier studies of the ultraviolet and visible spectra of adsorbed compounds, although none by the present simple method. De Boer and his collaborators<sup>5</sup> have investigated the absorption spectra of a number of compounds adsorbed on a transparent vacuum-sublimed film of an alkaline earth fluoride. The spectra of dyes adsorbed on colloids have been measured by Fodiman and Kargin<sup>6</sup>; the spectra vary with the relative charges of the colloidal particle and the dye ion. Several Russian investigators<sup>7-9</sup> have studied the spectra of a few select substances adsorbed on transparent silica gel, alumina and similar adsorbents. Weitz, Schmidt and Singer<sup>10</sup> have described the color changes which a variety of compounds undergo when adsorbed on silica gel and other adsorbents, and Meunier<sup>11</sup> has discussed briefly a few similar systems.

Recently Walling<sup>12</sup> and Benesi<sup>13</sup> have related visually observed color changes to the acid strengths of various catalyst surfaces.

### Experimental

Spectra were measured with a Cary Recording spectrophotometer, model 11 PMS. Because of the difficulty of working with slurries in conventional cells, special cells which easily could be disassembled and cleaned were built. The cell bodies were made of 0.3-cm. brass cut into a U-shape. Quartz windows were sealed to the cell bodies with Nonaq stopcock lubricant, a product of Fisher Scientific Company. Evaporation of the volatile cyclohexane was prevented by sealing L-shaped aluminum lids into the tops of the cells with Nonaq.

Slurries were prepared in the following manner: to 7.0 ml. of pure cyclohexane (for the reference cell) or cyclohexane solution (for the sample cell) was added 2.50 g. of silicic acid which had been heated at 160° for at least 18 hours before use. This heat treatment removed all physically absorbed water from the adsorbent.<sup>14</sup> In order to free the slurry of bubbles, it was stirred magnetically for two minutes with a glass-covered stirring bar. The concentration of the cyclohexane solution was adjusted to produce an absorbance of about 1.5 in a 0.3-cm. cell.

Since the spectra of solution and slurry were to be compared, it was desirable that the number of molecules of the absorbing species in the light path be the same in each case. First, an aliquot of the slurry was placed in the light path and the spectrum recorded. Then the corresponding solution spectrum was measured on a mixture of 7.0 ml. of solution with a volume of pure cyclohexane equal to the effective volume of the silicic acid added to the 7.0 ml. of solution used in preparing the slurry. The effective volume of the silicic acid used was estimated by measuring the increase in volume of 7.0 ml. of cyclohexane when 2.50 g. of silicic acid was stirred into it; this volume was found to be 1.1 ± 0.1 ml.

Because the molar absorptivities of most of the aromatic compounds were high, it was necessary to use very dilute solutions in order to obtain absorbances in the 1.0-1.5 range. Fortunately, even at low concentrations the solutes were approximately 100% adsorbed. Analysis of a slurry centrifugate of the least strongly adsorbed compound investigated, benzene, showed that only 8% of the solute present

remained unadsorbed. A similar experiment with the somewhat more polar diphenyl diselenide showed it to be essentially 100% adsorbed. Since all of the other compounds used were at least as polar as diphenyl diselenide, it was concluded that no corrections for unadsorbed material<sup>15</sup> would need to be applied to the slurry spectra.

Because the concentrations of the solutions employed were so low, ordinary impurities present in small concentration in the "pure" compounds were undetectable spectrophotometrically in the dilute solutions. Consequently, further purification of the reagent grade chemicals was usually unnecessary.

### Results and Discussion

Table I lists the wave lengths of maximum absorption of 22 aromatic compounds and the ratios of their absorptivities (at the maxima) in cyclohexane solution and adsorbed on activated silicic acid at the same concentration. The wave lengths of maximum absorption are also given for solid 4-nitrophenol and 4-nitroanisole imbedded in KBr disks.

Most of the effects observed in  $\pi$ - $\pi^*$ <sup>16</sup> transitions of mono-substituted benzenes on adsorption are in accord with conclusions drawn from Matsen's quantum mechanical treatment of the energy levels of mono-substituted benzenes.<sup>17</sup> Matsen finds that the energy difference between the highest filled orbital and the lowest vacant orbital decreases with increasing interaction between the "non-bonded" p<sub>z</sub> electrons in the substituent group and the  $\pi$ -electrons of the ring. The effects of adsorption on n- $\pi^*$  transitions are made reasonable by considering the interaction of the adsorbent with the non-bonded electrons in both the ground and excited states.

**Benzene.**—The 260 m $\mu$  transition in benzene is theoretically forbidden because of the sixfold symmetry of the  $\pi$ -electron system, but is partially allowed because of asymmetric vibrations of the carbon skeleton which introduce asymmetries in the  $\pi$ -system. If the silicic acid proton were to interact with the benzene  $\pi$ -electrons (at a point not on the sixfold axis), it would distort the system, lowering its symmetry, and a larger absorption intensity should result. Graphical integration of the present benzene spectra showed that the integrated absorption intensity appeared to decrease slightly (about 4%) on adsorption, but the effect is within the experimental error of the methods used and may not be significant. Bayliss and Hulme<sup>18</sup> have investigated the spectrum of benzene in water and cyclohexane and found the integrated absorption intensity was the same in both solvents.

It is possible that the interaction of an acidic proton with the  $\pi$ -electrons of benzene might contribute to the adsorption; acid-base interactions are now well known,<sup>19</sup> and indeed recently have

(5) E.g., J. H. de Boer and J. F. H. Custers, *Z. physik. Chem.*, **B25**, 238 (1934).

(6) E. V. Fodiman and V. A. Kargin, *J. Phys. Chem. (U.S.S.R.)*, **5**, 716 (1934).

(7) L. N. Kurbatov, *ibid.*, **14**, 1111 (1940).

(8) E. N. Pavlova, *Compt. rend. acad. Sci. (U.R.S.S.)*, **49**, 265 (1945).

(9) A. I. Terenin, *J. Phys. Chem. (U.S.S.R.)*, **14**, 1362 (1940).

(10) E. Weitz, F. Schmidt and J. Singer, *Z. Elektrochem.*, **46**, 222 (1940); **47**, 65 (1941).

(11) P. Meunier, *Compt. rend.*, **217**, 449 (1943).

(12) C. Walling, *THIS JOURNAL*, **72**, 1164 (1950).

(13) H. A. Benesi, *ibid.*, **78**, 5490 (1956).

(14) A. V. Kiselev, *Colloid J. (U.S.S.R.)*, **2**, 17 (1936).

(15) K. N. Trueblood, Ph.D. Thesis, California Institute of Technology, 1947.

(16) The electronic transition in which one of the mobile  $\pi$ -electrons in a  $\pi$ -electron system is excited to a vacant antibonding orbital, designated as  $\pi^*$ , is known as a  $\pi$ - $\pi^*$  transition; transitions designated as n- $\pi^*$  involve the excitation of a non-bonded (lone pair) electron in an atomic orbital to the  $\pi^*$  antibonding molecular orbital [M. Kasha, *Disc. Faraday Soc.*, **9**, 14 (1950)].

(17) F. A. Matsen, *THIS JOURNAL*, **72**, 5243 (1950).

(18) N. S. Bayliss and L. Hulme, *Australian J. Chem.*, **6**, 257 (1953).

(19) L. J. Andrews, *Chem. Revs.*, **54**, 713 (1954).

TABLE I  
 SPECTRAL DATA<sup>a</sup>

Compound	$\lambda_{\text{C}_6\text{H}_{12}}$ (m $\mu$ )	$\lambda_{\text{S.A.}}$	$\lambda_{\text{KBG}}$	$\epsilon_{\text{C}_6\text{H}_5/\text{ES.A.}}$
Aniline	288	274		1.9
	234	<235		
Anisole	278	274		
	271	268		
	265	262s		
Benzene	261	259	1.7	
	255	254	1.8	
	249	248	2.2	
	243	243	3.5	
Benzyl alcohol	265	263s		
	259	255		
	253	251		
Chlorobenzene	272	271	1.3	
	265	264	1.2	
	258	258s	1.0	
N,N-Dimethyl- aniline	298	?		
	251	237	4.7	
Diphenylamine	283-285	281		
Diphenyl diselenide	330-340	330	1.0	
	242-244	242-246	0.93	
Fluorobenzene	268	267	1.9	
	260	259	1.5	
	254	253	1.5	
	249	248s	1.9	
N-Methylaniline	294	276-278	2.7	
	244	<235		
2-Nitroaniline	375-378	413		
	270	285		
	246s	240		
	229			
4-Nitroaniline	323	374-382	3.6	
4-Nitroanisole	294	316	308-314	1.2
Nitrobenzene	253	271		1.3
4-Nitro-N-ethyl- aniline	344	420		
	~227			
4-Nitro-N,N-di- ethylaniline	360-366	420		
	234			
2-Nitrophenol	345-349	352-356		
	272	284-286		
4-Nitrophenol	286	315	325	1.3
Phenol	278	276		2.1
	271	270		1.7
	265	265s		1.4
Pyridine	276			
	261	261		0.71
	256	256		0.72
	251	251		0.88
Thiophenol	~280	~280		1.0
	254s			
	238	234		1.1
Triphenylamine	300	298		
	228s	<230		

<sup>a</sup> Spectral curves for a few of the compounds listed here are illustrated in *J. Chem. Ed.*, **33**, 526 (1956). <sup>b</sup> Abbreviations: C<sub>6</sub>H<sub>12</sub>, cyclohexane; S.A., silicic acid;  $\epsilon$ , absorptivity; s, shoulder.

been postulated as responsible for the selectivity of silica gels toward aromatic systems.<sup>20</sup> However, in view of the observed intensity effect, such an interaction seems at best rather weak in the present system.

(20) A. V. Kiselev, *Doklady Akad. Nauk S. S. S. R.*, **106**, 1046 (1956); *C. A.*, **50**, 11763 (1956).

Broadening and shifts to shorter wave lengths similar to those found for benzene on silicic acid as compared to cyclohexane solution were found with fluorobenzene, chlorobenzene and benzyl alcohol. The close similarity of the spectra of fluorobenzene, chlorobenzene and benzyl alcohol with that of benzene, both in cyclohexane and adsorbed on silicic acid, strongly suggests that the transitions in these molecules are of the same kind as in benzene, *i.e.*,  $\pi-\pi^*$ . If the transitions were  $n-\pi^*$ , then hydrogen bonding at the substituent group would be expected to alter the spectrum considerably on adsorption. In all cases, the shift amounted to about one per cent. of the total energy of the transition. A similar shift has been reported for the spectrum of benzene adsorbed on transparent silica gel from the vapor phase.<sup>8</sup> The broadening of the spectrum on adsorption has been interpreted as due to the statistical distribution of the energies of the benzene molecules in the field of the polar adsorbent.<sup>21</sup>

**Phenol and Anisole.**—The spectra of phenol and anisole in cyclohexane are almost identical; on silicic acid they are also approximately identical, at least in peak position. Both spectra are displaced to shorter wave lengths by about 2 m $\mu$ ; the relative intensities are not known. It seems likely that phenol acts both as a proton donor and acceptor when adsorbed on silicic acid; the  $pK_a$  of phenol is 9.9<sup>22</sup> while that of silicic acid is about 10,<sup>23</sup> and phenol is much more strongly adsorbed than similar ethers. Sporer<sup>24</sup> has found evidence that the heat of adsorption of phenol on silicic acid from benzene is about 2.5 kcal./mole greater than that of anisole and has suggested that this is because phenol can act both as a donor and as an acceptor in hydrogen bonds, while anisole can act only as an acceptor. Because the spectra of phenol and anisole are so similar while the extent of the interaction at the substituent group is quite different, and because their spectra behave so much like that of benzene, it is concluded that the electron being excited is one from the  $\pi$ -electron system and is not involved in the strong bonding to the adsorbent which probably occurs at the substituent group.

**Aniline.**—Two bands are observed in the spectrum of aniline in cyclohexane, corresponding to  $\pi-\pi^*$  and  $\pi-\pi^{**}$  transitions. The  $\pi^{**}$  is the second lowest vacant molecular orbital in the molecule. The spectrum of aniline in water shows both of these bands shifted to shorter wave lengths by 1000 cm.<sup>-1</sup>,<sup>25</sup> Here the water acts as a proton donor in a hydrogen bond; the aniline accepts the proton *via* the non-bonding electrons on the -NH<sub>2</sub> group. By partially isolating the 2p<sub>z</sub> electrons on the nitrogen atom, the hydrogen bond reduces the extent of the interaction between the 2p<sub>z</sub> electrons and the ring and thus shifts the absorption to shorter wave lengths.

(21) R. L. Sinsheimer, "Radiation Biology, Vol. II, Ultraviolet Radiations," National Research Council, A. Hollaender, Ed., McGraw-Hill Book Co., Inc., New York, N. Y., 1955, p. 169.

(22) I. M. Kolthoff and C. Rosenblum, "Acid-Base Indicators," The Macmillan Co., New York, N. Y., 1937, p. 383.

(23) L. Kay and K. N. Trueblood, *Anal. Chem.*, **26**, 1566 (1954).

(24) A. H. Sporer, Ph.D. Thesis, University of California, Los Angeles, 1956.

(25) L. Doub and J. M. Vandenbelt, *THIS JOURNAL*, **69**, 2714 (1947).

An increase in the acidity of the medium produced by adsorbing the aniline on silicic acid results in a further shift to shorter wave lengths, which can be attributed to the increased proton-donating ability of silicic acid relative to water.

In a solution of aniline in 0.1 *M* hydrochloric acid, the principal light-absorbing species is the anilinium ion rather than the aniline molecule. The previously non-bonding electrons are here intimately bound in a nitrogen-hydrogen bond and are thus unavailable for interaction with the ring. The spectrum in this case reverts to that of benzene. The effect on the energy levels of the decreasing *intramolecular* perturbation at the expense of increasing *intermolecular* interaction is shown graphically in Fig. 1, for aniline.

The *N*-alkylated anilines do not lend themselves to a ready explanation. Their absorption maxima are at longer wave lengths than that of aniline, indicative of increased interaction of the non-bonded electrons with the  $\pi$ -electrons of the ring, but they are also more basic than aniline.<sup>26</sup> These two properties appear contradictory.

**Pyridine.**—A satisfactory explanation of the changes in the pyridine spectrum on changing the solvent from a paraffin hydrocarbon to ethanol has been given by Halverson and Hirt.<sup>27</sup> The 276  $m\mu$  absorption band of pyridine in the hydrocarbon solvent is shifted to shorter wave lengths in ethanol and on silicic acid while the 256  $m\mu$  absorption remains unchanged on increasing the polarity of the medium. The 276  $m\mu$  transition of pyridine in a hydrocarbon solvent is assumed to involve the excitation of one of the non-bonded electrons (which are *not* in conjugation with the ring) on the nitrogen atom to the  $\pi^*$  molecular orbital. When pyridine is adsorbed on silicic acid the non-bonded electrons are stabilized in a hydrogen bond, *i.e.*, their ground state energy is lowered. In order to excite one of the non-bonded electrons in the hydrogen bonded pyridine molecule, it is necessary to supply not only the energy needed for excitation in the hydrocarbon solution but also an amount of energy sufficient to lift an electron out of the hydrogen bond, thereby disrupting it. The apparent disappearance of the 276  $m\mu$  band on silicic acid is thus seen to be the result of the shift of this band to shorter wave lengths where it is masked by the more intense  $\pi$ - $\pi^*$  transition at 256  $m\mu$ .

**Nitroaromatics.**—The absorption bands of nitroaromatic compounds are displaced to longer wave lengths when either the acidity of the medium is increased or groups which can act as electron donors in resonance with the nitro group are substituted on the ring.<sup>28</sup> Comparison of the spectra of 2- and 4-substituted nitroaromatic compounds in cyclohexane indicates that the bathochromic shift results from hydrogen bonding to the nitro group (or protonation of it, if the medium is a sufficiently strong acid). When the second substituent is a proton donor such as  $-\text{NH}_2$  or  $-\text{OH}$  and is in the position *ortho* to the nitro group, intramolecular hydrogen bonding shifts the absorption peak

(26) N. F. Hall and M. R. Sprinkle, *THIS JOURNAL*, **54**, 3469 (1932).

(27) F. Halverson and R. C. Hirt, *J. Chem. Phys.*, **19**, 711 (1951).

(28) W. A. Schroeder, P. E. Wilcox, K. N. Trueblood and A. O. Dekker, *Anal. Chem.*, **23**, 1740 (1951).

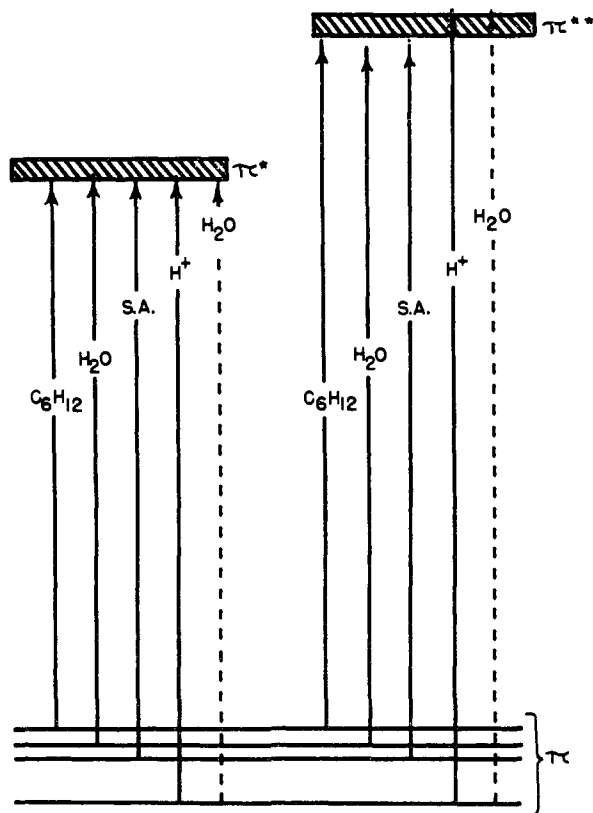


Fig. 1.—Energy level diagram: solid lines (transitions in aniline)  $\text{C}_6\text{H}_{12}$ , cyclohexane solution;  $\text{H}_2\text{O}$ , aqueous solution; S. A., adsorbed on activated silicic acid;  $\text{H}^+$ , anilinium ion in aqueous solution; dashed lines (transitions in benzene)  $\text{H}_2\text{O}$ , aqueous solution.

several thousand  $\text{cm}^{-1}$  to lower frequencies as compared to the *p*-substituted compound. Even more pronounced bathochromic shifts occur when these aromatic nitro compounds are adsorbed on activated silicic acid. Because similar displacements of the spectral bands are produced by chelation in *o*-substituted nitroaromatics and by dissolution of nitrobenzene and of *m*- and *p*-substituted nitroaromatics in proton-donating solvents, it seems reasonable to conclude that intermolecular hydrogen bonding is responsible for the latter displacements. The *N*-ethylated 4-nitroanilines show spectral shifts on adsorption which are qualitatively very similar to those of 4-nitroaniline itself. An earlier study with 4-nitroaniline in different media showed that the wave length of maximum light absorption decreased in the order: heated silicic acid > unheated silicic acid > aqueous ethanol > benzene.<sup>15</sup>

The ultraviolet spectrum of 4-nitrophenol in the crystalline state (imbedded in potassium bromide) was investigated because a shift of absorption to longer wave lengths, as compared to the spectrum in cyclohexane solution, was expected in view of the intermolecular hydrogen bonding undoubtedly present in the crystal. An appreciable shift was indeed found, but it is not unambiguously interpretable. Crystalline 4-nitroanisole also shows a large shift to longer wave lengths in spite of its

lack of acidic protons with which to form hydrogen bonds.

De Boer and Custers<sup>5</sup> have resolved the spectrum of 4-nitrophenol adsorbed on calcium fluoride into the spectrum due to absorption by the first monolayer of 4-nitrophenol, which is held by electrostatic forces, and the spectrum due to the subsequent layers of the compound, which are held by forces like those in the pure crystalline compound. The absorption attributed by them to the second and following layers corresponds well with our spectrum of 4-nitrophenol in potassium bromide.

Two applications of the present method for measuring spectra are immediately evident. Fieser<sup>29</sup> has suggested that the normally inert carcinogens are activated by adsorption onto genetic material in the cell. A most worthwhile investigation

(29) L. Fieser, National Academy of Sciences—National Research Council, Publication 206, Washington, D. C., 1951, pp. 384–385.

would be that of the spectra of the carcinogens in inert solvents and adsorbed on proteinaceous material and on nucleic acids. Michaelis and Granick<sup>30</sup> already have reported the spectra of histological stains adsorbed on colloidal suspensions of nucleic acid at pH 4.6.

Silica gels prepared in the presence of certain compounds and then extensively extracted show increased adsorption affinities for these compounds.<sup>31</sup> Gels prepared in this way retain a small amount of the adsorbate even under vigorous treatment and it would be worthwhile to investigate the firmly held adsorbate spectrophotometrically and compare its spectrum with that of the less firmly held adsorbate.

(30) L. Michaelis and S. Granick, *THIS JOURNAL*, **67**, 1212 (1945).

(31) F. H. Dickey, *J. Phys. Chem.*, **59**, 695 (1955).

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, NORTHWESTERN UNIVERSITY]

## The Exchange between Hydrocarbons and Deuterium on Palladium Catalysts<sup>1</sup>

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Results of isotopic exchange between deuterium and twelve alkanes and cycloalkanes are reported. Palladium on  $\gamma$ -alumina was principally employed as a catalyst but some work on evaporated palladium and rhodium films is included. At about 150°, the results on both palladium catalysts were similar and also resembled the results with nickel catalysts at this temperature rather closely. At temperatures below 100°, the impregnated palladium catalyst favors more extensive multiple exchange than does nickel. At 110–150°, nearly every molecule of (+)3-methylhexane which is exchanged is also racemized. At 60 to 80°, the initial isotopic exchange patterns of cyclopentane and cyclohexane exhibit marked discontinuities following the species of half-deuteration, cycloheptane exhibits a very small discontinuity and cyclooctane, none. Bicyclo[2.2.1]heptane exchanges only two hydrogen atoms in the initial step. These results are consistent with the assumption that *vic*-diadsorbed alkane (a state presumed to be equivalent to adsorbed olefin) occurs only in the eclipsed conformation.

Recent papers from this Laboratory<sup>2–4</sup> have reported the results of isotopic exchange reactions between deuterium and a number of different saturated hydrocarbons on a variety of nickel catalysts. In the present paper we report the results of a study of isotopic exchange between deuterium and twelve alkanes and cycloalkanes on palladium catalysts. The cycloalkanes: cyclopentane, methylcyclopentane, 1,1-dimethylcyclopentane, cyclohexane, cycloheptane, cyclooctane and bicyclo[2.2.1]heptane have led to results of considerable interest with respect to the mechanism of the exchange reaction and, in particular, of its stereochemistry.

### Experimental

**Materials.**—As the last steps in purification, hydrocarbons were fractionally distilled and percolated through silica gel.

Hexane, 2,3-dimethylbutane and heptane were Phillips Petroleum Co., pure grade. The preparations of 3,3-dimethylpentane and (+)3-methylhexane have been described.<sup>3</sup>

(1) Presented at the International Congress on Catalysis, Philadelphia, Pennsylvania, September 9, 1956.

(2) R. L. Burwell, Jr., and W. S. Briggs, *THIS JOURNAL*, **74**, 3096 (1952).

(3) H. C. Rowlinson, R. L. Burwell, Jr., and R. H. Tuxworth, *J. Phys. Chem.*, **59**, 225 (1955).

(4) R. L. Burwell, Jr., and R. H. Tuxworth, *ibid.*, **60**, 1043 (1956).

Cyclopentane and methylcyclopentane were Phillips research grades. The former was used as such but the latter contained a trace of impurity absorbing at 15  $\mu$  which was removed by percolation through silica gel. 1,1-Dimethylpentane supplied by the American Petroleum Institute, Project 45, and reported to have a purity of 99+ % was used as such.

Matheson cyclohexane was purified as described above. Cycloheptane was prepared by Wolff-Kishner reduction<sup>5</sup> of cycloheptanone (Geigy Pharmaceutical Co.), m.p. –8.0°. Cyclooctane was prepared by hydrogenation of cyclooctatetraene (Aldrich Chemical Co.), with platinum oxide in glacial acetic acid at room temperatures and 70 atm.; m.p. 14.3°.

Bicycloheptene<sup>6</sup> was hydrogenated with 70 atm. of hydrogen using nickel-kieselguhr (Harshaw) without solvent to give bicyclo[2.2.1]heptane; m.p. 86–87°. It would be safer to use a solvent to avoid the sudden exothermic hydrogenation which occurs when the autoclave is warmed to the melting point of bicycloheptene.

Purities as estimated by vapor phase chromatography are: cycloheptane, 99.7% or better; cyclooctane, 99.5%; bicycloheptane, 99.5%.

Electrolytic hydrogen was passed through a Deoxo unit (Baker and Co.) and a Dry Ice trap. Deuterium (Stuart Oxygen Company) was similarly purified.

A 3.3% palladium on  $\gamma$ -alumina was prepared by impregnation. A slurry of 26 g. of  $\gamma$ -alumina,<sup>7</sup> in a solution of 5.7 g. of palladium chloride in 100 cc. of water slightly

(5) Huang-Minton, *THIS JOURNAL*, **68**, 2487 (1946).

(6) C. L. Thomas, *Ind. Eng. Chem.*, **36**, 310 (1944).

(7) R. P. Eischens and P. W. Selwood, *THIS JOURNAL*, **69**, 1590 (1947).