

Addition of Symmetrical Diatomic Molecules to Benzene

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crete polyhedral groups with the required coordination, the polyhedra will be linked together sharing oxygen atoms. The oxygen content will determine the constitution of the groups formed by this linking together of the polyhedra and, consequently, the tendency to glass formation. In accordance with this, the glass forming

tendency in the systems of SiO_2 , B_2O_3 and P_2O_5 with basic oxides decreases with increasing content of basic oxide.

Finally, the author wants to thank Mr. H. Arnfelt of this Institute for many valuable discussions, which have contributed to the growth of the ideas appearing in this paper.

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Addition of Symmetrical Diatomic Molecules to Benzene

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The reaction of hydrogen and benzene to form 1,2-dihydrobenzene is considered, and the activation energy of the reaction is calculated with various assumptions concerning directed valence. It is shown that one may calculate approximate heats of reactions by considering exchange integrals only between electrons on neighboring atoms in a molecule, but this is not possible in calculating activation energies. The hydrogenation of benzene is considered as

an eight electron problem, and the system serves to illustrate the degree of simplification of the secular equation arising from the symmetry of the system. The matrix elements of the factored equation are calculated. Activation energies of the reactions involved in the adsorption of H_2 and C_6H_6 on Ni have been calculated and lead one to expect that the reaction might be achieved more easily catalytically.

INTRODUCTION

THE addition of a diatomic molecule to benzene is particularly interesting in that it involves a rearrangement of the six electrons in benzene which before reaction resonate chiefly between the two possible ways of drawing three double bonds (i.e., the Kekulé structures). After the addition reaction there are two conjugate double bonds.

Various aspects of the problem relating to benzene molecules have been discussed by Hückel,¹ Penney,² Pauling and Wheland,³ Seitz and Sherman,⁴ to mention only a few. However, the carrying through of an approximate calculation of the activation energy for a reaction of the type $\text{H}_2 + \text{C}_6\text{H}_6 \rightarrow \text{C}_6\text{H}_8$ has not been previously undertaken.

CALCULATION

a. Quantum mechanical considerations

In a reaction of the type $\text{H}_2 + \text{C}_6\text{H}_6 \rightarrow \text{C}_6\text{H}_8$ we consider eight electrons, one on each atom of the

diatomic molecule and the six in benzene which do not form unique bonds. The secular equation for eight electrons is of fourteenth degree, and we could, of course, use the fourteenth degree secular equation of Eyring and Kimball,⁵ in this case. But in the system we are considering, shown in Fig. 1, there is a plane of symmetry

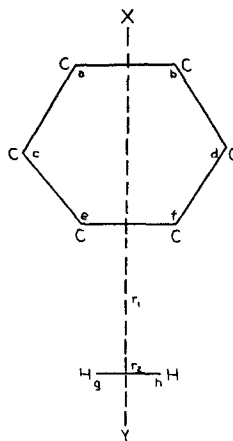


FIG. 1. Addition of H_2 to benzene to form 1,2-dihydrobenzene.

⁵ Eyring and Kimball, *J. Chem. Phys.* 1, 239 (1933).

* National Research Council Fellow in Chemistry, at the University of Wisconsin, 1933-34.

¹ Hückel, *Zeits. f. Physik* 70, 204 (1931).

² Penney, *Proc. Roy. Soc. A* 146 (1934).

³ Pauling and Wheland, *J. Chem. Phys.* 1, 362 (1933).

⁴ Seitz and Sherman, *J. Chem. Phys.* 2, 11 (1934).

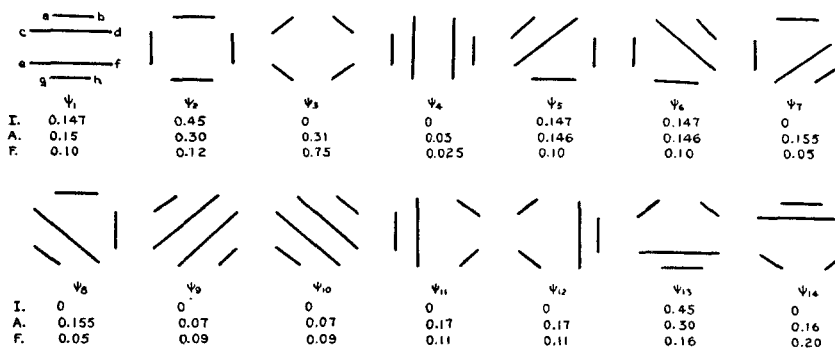


FIG. 2. The 14 linearly independent bond wave functions for 8 electrons with their coefficients in the wave function representing the initial activated and final state of the system H_2 and C_6H_6 for the reaction $H_2 + C_6H_6 \rightarrow 1,2$ -dihydrobenzene.

xy ,—i.e., if the system is rotated through 180° about the line xy the resulting system is physically identical with the original system. The rotation corresponds to sending a into b , b into a , c into d , d into c , etc. As we shall see, this symmetry enables us to factor our secular equation into a product of a tenth and a fourth degree equation.

The role which the symmetry of a system plays in factoring the secular equation has been formally discussed by Eyring, Frost and Turkevitch⁶ and by Seitz and Sherman.⁷ We therefore merely define wave functions which do factor the fourteenth degree equation, and calculate the corresponding matrix elements.

It was mentioned above that in general the secular equation for eight electrons is of fourteenth degree. This means that we express the wave function for the system as a linear combination of fourteen independent wave functions, i.e.,

$$\psi = \sum_{K=1}^{14} S_K \psi_K. \quad (1)$$

The fourteen functions $\psi_1, \psi_2, \dots, \psi_{14}$, that are used are the so-called bond wave functions.⁸ A convenient independent set is represented below in Fig. 2.

⁶ Eyring, Frost and Turkevitch, *J. Chem. Phys.* **1**, 777 (1933).

⁷ Seitz and Sherman, *J. Chem. Phys.* **2**, 11 (1934).

⁸ Sherman and Eyring, *J. Am. Chem. Soc.* **54**, 2661 (1932). Eyring and Kimball, *J. Chem. Phys.* **1**, 239 (1933).

The diagram of the wave function ψ_1 indicates the position of the atoms for the other wave functions also. For any configuration of the atoms the actual wave function for the system H_2 +benzene is some linear combination of the independent set of fourteen. The coefficients which multiply the wave functions for the initial state (with the H_2 molecule remote from the benzene), the final state of dihydrobenzene, and the intermediate activated state are indicated in the appropriate rows beneath each wave function.

It is perhaps well to point out that it is meaningless in the chemical sense to speak of the system having at a particular moment a particular pure bond state. This is because no chemical experiment can be designed which would show the system to oscillate between the fourteen ways of drawing the bonds, since the passage from one bond structure to another involves motion of electrons which, because of their small mass, pass through all the bond states during a time interval in which atomic nuclei (the test bodies of chemistry) do not move appreciably. Thus the potential energy of an atomic system depends only on the averaged position of the electrons, and this is given by the linear combination of the fourteen bond wave functions appropriate to the particular atomic configuration.

The manner in which atoms are bonded is in a certain sense a much less fundamental chemical concept than the energy of the corresponding

configuration. It is, for example, the energy which enters into the thermodynamic and rate equations describing the behavior of chemical systems. In fact, the interest in the manner of binding is about proportional to the extent to which it summarizes energy relations. It is this same fact which makes energy surfaces so fundamentally interesting.

Suppose, now, instead of using the fourteen wave functions given in Fig. 2 we define a new set of fourteen as follows:

$$\begin{aligned}\phi_1 &= \psi_1, & \phi_6 &= \psi_7 + \psi_8, & \phi_{11} &= \psi_5 - \psi_6, \\ \phi_2 &= \psi_2, & \phi_7 &= \psi_9 + \psi_{10}, & \phi_{12} &= \psi_7 - \psi_8, \\ \phi_3 &= \psi_3, & \phi_8 &= \psi_{11} + \psi_{12}, & \phi_{13} &= \psi_9 - \psi_{10}, \\ \phi_4 &= \psi_4, & \phi_9 &= \psi_{13}, & \phi_{14} &= \psi_{11} - \psi_{12}, \\ \phi_5 &= \psi_5 + \psi_6, & \phi_{10} &= \psi_{14},\end{aligned}$$

This set of fourteen wave functions possesses the property of falling into two non-combining sets of ten and four, i.e., the matrix element

$$\int \phi_i H \phi_j d\tau = 0$$

if $i = 1, 2, 3, \dots, 10$ and $j = 11, 12, 13$, or 14 .

This of course means that the fourteenth degree secular equation factors into a product of a tenth and fourth degree equation, so that for any system of eight electrons possessing the symmetry of Fig. 1 we need only solve a tenth degree equation. In the calculation of activation energies we are interested in finding the lowest of the fourteen roots and since this lies in the tenth degree equation, we need only be concerned with it.

The wave functions $\phi_1, \phi_2, \dots, \phi_{10}$ do not form an orthogonal set ($\int \phi_i \phi_j d\tau \neq 0$ when $i \neq j$), but a new set, formed from a linear combination of the ϕ 's, may be found which are orthogonal,—and, hence more tractable. These are defined below in Table I and the matrix components between them given in Table II.

TABLE I.

$$\begin{aligned}\chi_1 &= \phi_1 \\ \chi_2 &= \phi_2 - 1/2\phi_1 \\ \chi_3 &= \phi_3 - 1/2\phi_1 \\ \chi_4 &= \phi_4 - \phi_3 - \phi_2 + 1/2\phi_1 \\ \chi_5 &= \phi_5 - 1/2\phi_1 \\ \chi_6 &= \phi_6 - \phi_5 - \phi_2 + 1/2\phi_1 \\ \chi_7 &= \phi_7 - 1/2\phi_6 - 1/2\phi_3 + 1/4\phi_1 \\ \chi_8 &= \phi_8 - \phi_7 - 1/2\phi_4 + 1/2\phi_5 - 1/2\phi_3 + 1/2\phi_2 - 1/4\phi_1 \\ \chi_9 &= \phi_9 + 3/5\phi_8 - 8/5\phi_7 - 4/5\phi_6 + 4/5\phi_5 - 4/5\phi_4 \\ &\quad + 4/5\phi_3 + 4/5\phi_2 - 2/5\phi_1 \\ \chi_{10} &= \phi_{10} - 3/4\phi_9 - 1/4\phi_8 + 2/3\phi_7 + 1/2\phi_6 - 1/3\phi_5 \\ &\quad + 1/2\phi_4 - 1/3\phi_3 - \phi_2 + 1/6\phi_1\end{aligned}$$

b. Activation energies

The tenth order secular equation given in Part *a* was used to calculate the activation energies of several reactions involving the configurations of eight electrons. This was done in the usual way by constructing a potential energy surface.⁹ The various exchange and coulombic integrals were evaluated as usual, by constructing morse potential energy curves for the various bonds involved.

Let us now consider the reaction $C_6H_6 + H_2 \rightarrow C_6H_8$ in some detail. The calculations correspond to the approach of H_2 to benzene in a plane making such an angle with the plane of the benzene ring as corresponds to that existing in 1,2-dihydrobenzene. At the beginning of the reaction the distance r_1 of Fig. 1 is very large and r_2 has the value for the normal distance between hydrogen atoms in H_2 . As the reaction proceeds r_1 decreases and r_2 increases. If the various integrals involved are evaluated from Morse potential energy curves, which involves the assumption that the value of these integrals is a function only of the distance between atoms, a potential energy surface results which gives an activation energy for the reaction of 95.6 kg cal. and a value for the heat of the reaction, $\Delta H = +85.1$ kg cal., i.e. 1,2-dihydrobenzene is 85.1 kg cal. less stable than $H_2 + \text{benzene}$. Thermochemical data indicate that 1,2-dihydrobenzene is slightly more stable than $H_2 + \text{benzene}$.

Now Pauling and Wheland¹⁰ and Pauling and Sherman¹¹ have calculated heats of reaction,—or, rather, resonance energies—of a large number of organic molecules, and assumed the exchange integral between all pairs of electrons other than those on neighboring atoms is zero, and obtained quite satisfactory results, as judged by numerical agreement. Their assumption is equivalent to saying that the wave functions of electrons on atoms in polyatomic molecules do not possess the spatial symmetry existing in atoms forming

⁹ Eyring and Polanyi, *Zeits. f. physik. Chemie* **B12**, 279 (1931); Eyring, *J. Am. Chem. Soc.* **53**, 2537 (1931); Sherman and Eyring, *ibid.* **54**, 2661 (1932); Kimball and Eyring, *ibid.* **54**, 3876 (1932); Eyring, Sherman and Kimball, *J. Chem. Phys.* **1**, 586 (1933).

¹⁰ Pauling and Wheland, *J. Chem. Phys.* **1**, 362 (1933).

¹¹ Pauling and Sherman, *ibid.* **1**, 606 (1933).

TABLE II.

	H _{1,1}	H _{1,2}	H _{1,3}	H _{1,4}	H _{1,5}	H _{1,6}	H _{1,7}	H _{1,8}	H _{1,9}	H _{1,10}	H _{2,1}	H _{2,2}	H _{2,3}	H _{2,4}	
C	1	0	0	0	0	0	0	0	0	0	3/4	0	0	0	
ab	0	3/2	3/2	0	0	0	0	3/4	6/5	0	0	0	0	3/4	
ad	-3	-3/2	-3/2	-3/2	0	0	0	-3/4	-6/5	0	-3/4	-3/4	-3/4	-3/4	
af	0	0	0	3/2	0	0	0	0	0	0	-3/2	3/4	0	0	
ag	-1	0	0	0	3/2	0	0	0	0	0	-3/4	0	0	0	
ah	-1	0	0	0	0	-3/2	0	0	0	0	-3/4	0	0	0	
cg	-1	0	0	0	0	0	0	3/4	6/5	0	-3/4	0	0	0	
ch	-1	0	0	0	-3/2	0	0	0	0	0	-3/4	0	0	0	
eg	-1	0	0	0	0	3/2	0	0	0	0	-3/4	0	0	0	
eh	-1	0	0	0	0	0	0	-3/4	-6/5	0	-3/4	0	0	0	
gh	1	0	0	0	0	0	0	0	0	0	3/4	0	0	0	
	H _{2,5}	H _{2,6}	H _{2,7}	H _{2,8}	H _{2,9}	H _{2,10}	H _{3,1}	H _{3,2}	H _{3,3}	H _{3,4}	H _{3,5}	H _{3,6}	H _{3,7}	H _{3,8}	H _{3,9}
C	0	0	0	0	0	0	3/4	0	0	0	0	0	0	0	0
ab	3/4	-3/4	-3/8	3/8	0	-1/4	0	3/4	0	0	0	0	0	0	-27/20
ad	-3/2	3/2	3/4	-3/4	-3/5	1/2	-3/4	-3/4	0	0	0	0	0	0	21/10
af	3/4	-3/4	-3/8	3/8	3/5	-1/4	-3/2	0	0	0	0	0	0	0	0
ag	-3/4	3/2	3/8	-3/8	-3/5	1/4	-3/4	0	0	0	0	9/8	0	0	0
ah	0	-3/4	-3/8	3/8	3/5	-1/4	-3/4	0	0	0	0	0	-3/8	-3/5	0
cg	0	0	3/8	-3/4	-3/10	5/8	-3/4	0	0	3/4	0	0	0	0	-27/20
ch	3/4	-3/2	-3/8	3/8	3/5	-1/4	-3/4	0	0	0	-9/8	0	0	0	0
eg	0	3/4	3/8	-3/8	-3/5	1/4	-3/4	0	0	0	0	3/8	3/5	3/5	0
eh	0	0	-3/8	3/4	3/10	-5/8	-3/4	0	0	-3/4	0	0	0	3/5	0
gh	0	0	0	0	0	0	3/4	0	0	0	0	0	0	0	0
	H _{3,10}	H _{4,1}	H _{4,2}	H _{4,3}	H _{4,4}	H _{4,5}	H _{4,6}	H _{4,7}	H _{4,8}	H _{4,9}	H _{4,10}	H _{5,1}	H _{5,2}	H _{5,3}	H _{5,4}
C	0	3/4	0	0	0	0	0	0	0	3/4	0	0	0	0	0
ab	9/16	-3	-3/4	3/4	-3/8	3/8	27/20	-13/16	-3/2	0	7/8	-3/8	-6/5	-6/5	0
ad	-9/8	-3/4	3/2	-3/2	3/4	-3/4	-21/10	13/8	-9/4	3/4	-7/8	-9/8	-6/5	-6/5	0
af	0	3/2	-3/4	3/4	3/8	-3/8	-6/5	1/4	0	-3/4	0	3/2	12/5	12/5	0
ag	0	-3/4	3/4	-3/4	-3/8	3/4	9/5	-1/4	3/4	3/4	0	-3/8	-3/5	-3/5	0
ah	0	-3/4	-3/4	3/4	0	-9/8	-3/10	-3/8	-3/4	-3/4	0	3/8	3/5	3/5	0
cg	9/16	-3/4	3/4	0	-3/4	3/4	15/4	-17/16	-3/4	0	0	0	-3/5	-3/5	0
ch	0	-3/4	-3/4	3/4	3/8	-3/4	-9/5	1/4	3/4	-3/4	0	3/8	3/5	3/5	0
eg	0	-3/4	3/4	-3/4	0	9/8	3/10	3/8	-3/4	3/4	0	-3/8	-3/5	-3/5	0
eh	0	-3/4	-3/4	0	0	0	-9/5	0	-3/4	0	0	0	3/5	3/5	0
gh	0	3/4	0	0	0	0	0	0	-3/4	0	0	0	0	0	0
	H _{5,10}	H _{6,1}	H _{6,2}	H _{6,3}	H _{6,4}	H _{6,5}	H _{6,6}	H _{6,7}	H _{6,8}	H _{6,9}	H _{6,10}	H _{7,1}	H _{7,2}	H _{7,3}	H _{7,4}
C	0	3/4	0	0	0	0	9/16	0	0	0	15/16	0	0	0	0
ab	0	3/2	-3/8	3/4	9/5	-1/4	-9/8	3/16	11/40	-33/32	-21/4	-201/40	21/8	-3/4	-3/4
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af	-3/2	0	3/2	-3/2	-27/5	23/8	-9/8	-3/16	-3	9/8	3/16	33/10	-17/8	-17/8	0
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ah	-3/4	9/4	3/8	-2	-22/5	1	-9/16	3/4	-3/10	3/8	5/4	11/4	-5/8	-5/8	0
cg	0	3/4	0	5/8	13/10	0	-9/16	-3/8	63/40	-27/32	-19/16	-61/40	9/8	9/8	0
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eh	0	-3/4	0	-5/8	-13/10	0	-9/16	-3/4	0	0	1/16	17/20	-5/16	-5/16	0
gh	0	-3/4	0	0	0	0	-9/16	0	0	0	-15/16	0	0	0	0
	H _{8,9}	H _{8,10}	H _{10,10}	H _{11,11}	H _{11,12}	H _{11,13}	H _{11,14}	H _{12,12}	H _{12,13}	H _{12,14}	H _{13,13}	H _{13,14}	H _{14,14}	H _{14,15}	H _{14,16}
C	3/5	0	5/16	3/2	0	0	0	3/2	0	0	3/4	0	0	3/4	3/4
ab	-216/25	47/10	-101/32	-3	0	0	0	-3/2	3/4	3/4	-9/4	-3/2	-3/2	-3/4	-3/4
ad	-117/25	-13/5	5/8	0	0	0	0	-3	-3/2	0	-3/2	0	0	-9/4	-9/4
af	102/25	-73/20	7/4	-3/2	0	0	0	-3	3/4	-3/4	0	3/2	0	-3/4	-3/4
ag	-128/25	1	-11/8	-3/2	0	3/4	-3/4	0	0	0	0	0	0	0	0
ah	41/10	-13/8	35/32	-3/2	0	-3/4	-3/4	0	0	0	-3/4	-3/4	0	0	0
cg	-167/50	107/40	-5/4	-3/2	-3/2	0	0	-3/2	0	0	0	0	0	0	0
ch	104/25	-1	1/8	-3/2	0	-3/4	3/4	0	0	0	-3/4	3/4	0	-3/4	-3/4
eg	-259/50	3/8	-5/32	-3/2	0	3/4	3/4	0	0	0	0	0	0	-3/4	-3/4
eh	53/50	1/8	5/32	-3/2	3/2	0	0	-3/2	0	0	0	0	0	0	0
gh	-3/5	0	-5/16	3/2	0	0	0	-3/2	0	0	-3/4	0	0	-3/4	-3/4

diatomic molecules,—assumed by us in the above calculation. In other words, the value of the exchange integral between electron pairs in polyatomic molecules is not simply a function of the distance between atoms but also of *direction*, i.e., directed valence is considered.

If we consider exchange integrals between electrons on non-neighboring atoms to be zero the value of ΔH drops to +26.1 kg cal.—in much better agreement with experiment. The fact that ΔH is still positive is primarily due to

the incorrect (too small) C—H bond energy used in the calculation (see below).

It is to be emphasized that, although it has just been shown that it is much better to consider interactions between electrons on neighboring atoms only, for the initial and final state of the system, it is absolutely unsatisfactory to do so for the *whole* potential energy surface. Thus, if we consider interactions between electrons on neighboring atoms only, the calculated activation energy for the hydrogenation of

benzene to form 1,2-dihydrobenzene drops from 95.6 kg cal. to 36.6 kg cal. This is obviously too low (if a stronger C—H bond energy were used it would be even lower), as is realized when one recalls that the activation energy for the hydrogenation of C_2H_4 , a more readily achieved reaction, is 43.3 kg cal. Also, the hydrogenation of benzene is carried out at catalytic surfaces at temperatures as high as 500–550°K, which means that in this temperature range the gas-phase reaction must still be relatively slow, corresponding to an activation energy greater than 40 kg cal.

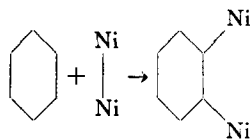
Another assumption that might be made—more reasonably perhaps, than to consider only interactions between electrons on neighboring atoms—is to set all non-neighboring interactions equal to zero except *eh* and *fg*. This gives an activation energy of 84.5 kg cal. If one neglected the electrons *a*, *b*, *c*, and *d* altogether, this being equivalent to considering the reaction as a four electron problem, the reaction would then be essentially the same as $C_2H_4 + H_2 \rightarrow C_2H_6$. All the experimental evidence, however, points to the latter reaction as being more easily achieved. Also, the heats of two reactions differ considerably.

The fact that directed valence is operative in polyatomic molecules probably accounts for the fact that the discrepancy between the calculated and experimental value for the activation energy is almost always such that the difference between calculated and experimental value is almost always positive, but the fact that this difference is small indicates the method used so far is approximately correct.

From what has been said above, it follows that the best semi-empirical method of calculating a potential energy surface for the reaction $C_6H_6 + H_2 \rightarrow C_6H_8$ is to do so by considering non-neighboring exchange integrals zero except *eh* and *fg*. This was done, by using a C—H bond strength of 120 kg cal., and a heat of reaction $\Delta H = -11$ kg cal. We consider these values to be the most reliable.^{11a}

^{11a} The value of 120 kg cal. for a C—H bond is for the diatomic molecule. The much lower observed values in compounds is a consequence of the repulsive interaction with the other groups attached to the carbon.

The activation energy of the reaction



was calculated in a manner similar to the one just described for the addition of H_2 to benzene, except that the percentage of coulombic binding in Ni—C was taken to be 22,—in qualitative accord with the known result that this percentage increases for metallic bonds.¹² With this assumption the calculated activation energy is found to be 3 kg cal., and $\Delta H = -5$ kg cal.

The activation energy of the reaction $H_2 + Ni_2 \rightarrow 2 Ni-H$ was calculated in the usual manner, assuming the reaction involves the configuration of four electrons, one on each of the four atoms. The percentage of coulombic binding in Ni—H was taken as 20, and in Ni—Ni as 30. The activation energy was found to be 24 kg cal., and $\Delta H = -4.6$ kg cal.

RESULTS

The results of all the calculations are summarized in Table III.

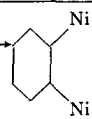
DISCUSSION

The experimental data concerning the rate of the homogeneous gas-phase addition of H_2 to benzene are extremely meager and indirect. One cannot deduce a numerical value for the activation energy from the numerical data. As already mentioned, about all one can say is that it is high,—greater than 40 kg cal. The calculated value, therefore, is of the right order of magnitude. It shows that the homogeneous gas-phase addition of H_2 to benzene is impractical because, at the high temperature necessary to cause the reaction to have an appreciable rate, equilibrium would be against it.

From Table III it is seen that the calculated value of the activation energy is very much less sensitive to the various assumptions made than

¹² Bartlett and Furry, Phys. Rev. 37, 1712 (1931), for example, show this percentage is 22 for Li_2 , and Rosen, Phys. Rev. 38, 255 (1931), calculates it to be 28.3 in Na_2 .

TABLE III.

Reaction	Bond	Constants			Assumptions (see Fig. 1)	ΔH kg cal.	A kg cal.
		r_0 Å	ω_0 cm ⁻¹	D kg cal.			
$C_6H_6 + H_2 \rightarrow C_6H_8$	H-H C-H	0.74	4375	102.4	a. All integrals evaluated from Morse P.E. curves. Coulombic energy = 14%.	+85.1	95.6
		1.12	2930	92.3	b. Exchange integrals between all electron-pairs = 0 except <i>ab</i> , <i>bd</i> , <i>df</i> , <i>ef</i> , <i>ce</i> , <i>ac</i> , <i>eg</i> , <i>fh</i> , and <i>gh</i> . These are determined as in <i>a</i> .	+26.1	36.6
					c. Same as <i>b</i> except <i>eh</i> and <i>fg</i> ≠ 0.		84.5
	H-H C-H	0.74 1.12	4375 2930	102.4 120.0	Same as <i>c</i> above.	-11	78.3
$C_6H_6 + Ni-Ni \rightarrow$ 	Ni-C	1.92		60	Same as <i>c</i> above, except that for the Ni-C bond the coulombic energy was taken as 22% of bond energy, and for Ni-Ni bond as 30%.	-5	3
	Ni-Ni	2.38		20			
$H_2 + Ni_2 \rightarrow 2Ni-H$	Ni-Ni	2.38		20	This reaction involves the configuration of 4 electrons, and was considered in the usual way.	-4.6	24
	Ni-H	1.56		66.2			

is the heat of the reaction. Thus, while the activation energy changes from 95.6 to 78.3 kg cal. the heat of the reaction changes from +85.1 to -11 kg cal. Thus, although there is frequently considerable uncertainty in bond strengths, the corresponding error in the activation energy is considerably less.

It is interesting to calculate the coefficients of Eq. (1) for the system C_6H_6 and H_2 , using the wave functions of Fig. 2, for the initial, activated, and final states of the reaction $C_6H_6 + H_2 \rightarrow C_6H_8$. The results are given in Fig. 2, in the rows below the wave functions.

The value of the coefficients shows that the chemical reaction may be thought of as passing from an initial state where there is a fairly definite way of drawing the valence bonds (the Kekulé structures for benzene), through an activated state where one cannot represent the system even approximately by any particular way of drawing the bonds, to a final state where one can represent the system to a good approximation by a unique way of drawing the bonds. Thus, in the initial state the system may be represented approximately by $\psi = s_2(\psi_2 + \psi_{12})$, and in the final state by $\psi = s_3\psi_3$, but at the activated state

one must include at least $\psi_1, \psi_2, \psi_3, \psi_5, \psi_6, \psi_7, \psi_8, \psi_{11}, \psi_{12}, \psi_{13}$ and ψ_{14} .

It is interesting to compare the calculated activation energy values for the hydrogenation of ethylene, butadiene, and benzene. The activation energy rapidly increases in going from C_2H_4 to C_6H_6 , as, perhaps, would be expected. The hydrogenation of 1,2-dihydrobenzene would be closely analogous to that of butadiene, and of cyclohexane to that of ethylene, so that if benzene could be hydrogenated homogeneously one would expect the product to be cyclohexane and not 1,2-dihydrobenzene because the third molecule of H_2 would, at a given temperature,

TABLE IV.

Reaction	Activation energy (calc.)
$H_2 + C_2H_4 \rightarrow C_2H_6$	43.5 ¹³
$H_2 + CH_2=CH-CH=CH_2$ $\rightarrow CH_3-CH=CH-CH_3$	65.0 ¹⁴
$H_2 + C_6H_6 \rightarrow C_6H_8$	78.5

¹³ Sherman and Eyring, J. Am. Chem. Soc. 54, 2661 (1932). The value given in this paper is based on 10 percent coulombic energy, and that given above is based on 14 percent coulombic energy.

¹⁴ Eyring, Sherman and Kimball, J. Chem. Phys. 1, 586 (1933).

enter the benzene nucleus more rapidly than the second molecule of H_2 , which in turn would enter more rapidly than the first molecule. If this same relative order of activation energies held for the surface reactions one would also expect cyclohexane to be the product obtained upon catalytically hydrogenating benzene. This is apparently the case, although the surface reaction mechanism may be such that the separate steps are indistinguishable.¹⁵

The activation energies calculated for the reactions involving Ni are probably not very

precise, but it is undoubtedly of significance that they are all of a lower order of magnitude than that for the hydrogenation of benzene. Thus, one might expect that, at least insofar as the rates of adsorption and desorption of H_2 and benzene on it are rate-determining, the hydrogenation of benzene could be achieved more easily on a catalytic nickel surface. This is experimentally the case, as was shown by Sabatier¹⁶ and studied in detail by Dougherty and Taylor.¹⁷ The latter authors found the catalytic reaction to be rapid from 60°C to 200°C.

¹⁵ For example, see Ballandin, *Zeits. f. physik. Chemie* **B2**, 289 (1929).

¹⁶ Sabatier, *Ind. Eng. Chem.* **18**, 1006 (1926).

¹⁷ Dougherty and Taylor, *J. Phys. Chem.* **27**, 533 (1923).

The Dipole Moments of Certain Monosubstituted Benzenes in the Vapor State

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The dielectric constants of the vapors of three monosubstituted benzenes have been determined over a range of temperature and used to calculate dipole moments as follows: fluorobenzene, 1.57×10^{-18} ; chlorobenzene, 1.70×10^{-18} ; nitrobenzene, 4.19×10^{-18} . These values are considerably higher than those found from previous measurements in solution and agree well with values calculated for the vapor state by the application of an empirical equation developed by Müller to measurements in solution.

THESE measurements were made nearly two years ago in an attempt to obtain reliable values for the moments of certain common dipoles which are frequently used in studies of molecular structure. They have taken on added interest because of recent work upon the dependence of the apparent value of a moment measured in solution upon the dielectric constant of the solvent.

The dielectric constants were measured with the apparatus previously described.¹ For fluorobenzene and chlorobenzene, the polarization P was calculated from the dielectric constant ϵ and the molar volume V as $P = [(\epsilon - 1)/(\epsilon + 2)]V$, the polarization-pressure curve at each absolute temperature T being extrapolated to zero pressure to obtain a value P_0 for use in the Debye equation, $P = a + b/T$. The value of the atomic

polarization was calculated as $P_A = a - P_E$, the difference between a , the total induced polarization, and P_E , the molar refraction extrapolated to infinite wavelength. The dipole moments were calculated from the values of b as $\mu = 0.01273 \times 10^{-18}(b^{1/2})$ and should be in error by no more than 0.01×10^{-18} .

The same procedure in the case of nitrobenzene, which had to be measured at lower pressures than the other two substances gave a value 4.03×10^{-18} and the abnormally large value 20.5 for the atomic polarization. When the moment was calculated at each temperature by subtracting P_E from the total polarization at zero pressure, values were obtained which rose from 4.20 to 4.25×10^{-18} with rising temperature. As it appeared probable that greater errors arose from extrapolating to zero pressure the polarizations at pressures below 200 mm than from deviations from the gas laws, the polarizations

¹ McAlpine and Smyth, *J. Am. Chem. Soc.* **55**, 453 (1933); *J. Chem. Phys.* **2**, 499 (1934).