

ENERGY CHANGES INVOLVED IN THE ADDITION REACTIONS OF UNSATURATED HYDROCARBONS

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This paper is in the nature of a progress report. It is an attempt to survey from the point of view of the organic chemist the data which have recently been obtained in the course of a series of thermochemical studies in the Harvard laboratories (3). The aim of these studies is to measure directly the heat changes involved in chemical reactions, in particular addition reactions of all manner of unsaturated and cyclic compounds. It is usually possible to obtain much more accurate data by such direct measurements than by calculating the heat effect of an addition reaction from heats of combustion. This is particularly true, of course, in the case of compounds containing a considerable number of carbon atoms whose heat of combustion is large and where in calculating the heat of addition of two hydrogen atoms, for example, one must take the difference of two large numbers. Although the program outlined is in its first stages, a number of interesting results have already been obtained which seem to throw considerable light on a number of problems of the organic chemist. For this reason, it seems worth while to present this summary of the work, incomplete as it is, and to point out some of the questions which await solution.

In table 1 are collected all the data which have been obtained thus far in the direct determination of the heats of hydrogenation. These measurements are all made for gas-phase reactions. For the experimental details in regard to the adiabatic calorimeter used, the method of measurement, and the purification of the compounds, the reader may consult the original papers. In general the accuracy of the data is of the order of 0.1 to 0.3 per cent. The table is divided into sections according to the number of hydrogen atoms involved in the addition reaction whose heat was measured.

Considering, first, section A of table 1 it is evident that the substitution of the hydrogen atoms of ethylene by alkyl groups diminishes the heat evolved in the hydrogenation. This effect reaches its maximum in the compounds measured in the case of tetramethylethylene with which 6.2

Cal. less heat is evolved in hydrogenation than in the case of the parent hydrocarbon. However, the effect of progressively substituting the four hydrogen atoms by methyl groups is not additive, but on the contrary each subsequent alkyl group is less effective than the preceding one. The

TABLE I
Heats of hydrogenation of unsaturated and aromatic compounds at 82°C. (355°K.) (ΔH)
in large calories

| COMPOUND | ΔH | COMPOUND | ΔH |
|---------------------------------------|------------|--------------------------------|------------|
| A. Addition of H ₂ | | | |
| Ethylene..... | -32.8 | <i>as</i> -Methylethylene..... | -28.5 |
| Propylene..... | -30.1 | Pentene-2 (mixture)..... | -28.0 |
| Butene-1..... | -30.3 | Cyclopentene..... | -26.9 |
| Heptene-1..... | -30.1 | Cyclohexene..... | -28.6 |
| Isopropylethylene..... | -30.3 | Trimethylethylene..... | -26.9 |
| Tertiary-butylethylene..... | -30.3 | Tetramethylethylene..... | -26.6 |
| Neopentylethylene..... | -29.5 | Vinyl acetate..... | -31.1 |
| Isobutene..... | -28.4 | Crotonaldehyde..... | -25.2 |
| Butene-2 (<i>trans</i>)..... | -27.6 | 2-Ethoxypropene..... | -25.1 |
| Butene-2 (<i>cis</i>)..... | -28.6 | Acetone..... | -13.4 |
| <i>as</i> -Methylisopropylethylene... | -28.0 | Methyl ethyl ketone..... | -13.2 |
| B. Addition of 2H ₂ | | | |
| Allene..... | -71.3 | Limonene*..... | -54.1 |
| Butadiene-1,3..... | -57.1 | α -Phellandrene*..... | -53.4 |
| 2,3-Dimethylbutadiene-1,3.... | -53.9 | α -Terpinene*..... | -50.7 |
| Pentadiene-1,3..... | -54.1 | Pentadiene-1,4..... | -60.8 |
| Cyclohexadiene-1,3..... | -55.4 | Hexadiene-1,5..... | -60.5 |
| Cyclopentadiene-1,3..... | -50.9 | Furane..... | -36.6 |
| | | Divinyl ether..... | -57.2 |
| C. Addition of 3H ₂ | | | |
| Benzene..... | -49.8 | <i>o</i> -Xylene..... | -47.3 |
| Ethylbenzene..... | -48.9 | Dihydroindene..... | -45.8 |
| Mesitylene..... | -47.6 | | |
| D. Addition of 4H ₂ | | | |
| Styrene..... | -77.5 | Indene..... | -69.9 |

* Compounds of somewhat uncertain purity.

jump from ethylene to propylene, for example, is 2.7 Cal., while that from trimethylethylene to tetramethylethylene is only 0.3. A comparison of propylene, butene-1, heptene-1, tertiary-butylethylene, neopentylethylene and isopropylethylene shows that within a few tenths of a Calorie the

methyl, ethyl, *n*-amyl, isopropyl, tertiary-butyl, and neopentyl groups are equally potent in decreasing the affinity of the double bond for hydrogen. The differences between these compounds, while greater than the experimental error, are clearly second-order effects compared to the action of an alkyl group in general. The three compounds of the type $R_2C=CH_2$ which have been measured give the same value for $-\Delta H$ of hydrogenation (28.2) within 0.2 Cal., and this value is almost the same as that for *cis*-butene-2 ($CH_3CH=CHCH_3$) (28.6). Here again, omitting a consideration of second-order effects, two alkyl groups in the α, α - or α, β -position (if *cis*) produce essentially the same effect. These generalizations seem to apply to simple primary and secondary alkyl groups and less accurately to the more highly branched ones.¹

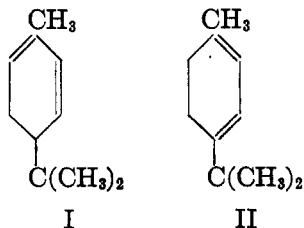
The difference of 1.0 Cal. between the *cis*- and *trans*-forms of butene-2 is striking, the *cis*-form having the greater affinity for hydrogen as measured by the total energy change. The value of cyclohexene is practically identical with that of *cis*-butene-2, as would be expected. Cyclopentene, however, is less unsaturated by 1.7 Cal.; this fact will be referred to later.

We may now consider the effect of a multiplicity of double linkages. Sections B and D of table 1 at first sight reveal a number of interesting regularities. The very large value of allene being considerably more than twice the figure for ethylene shows that this compound may be considered the most highly unsaturated compound yet examined by these methods. A comparison of the three compounds of the type $CH_2=CH(CH_2)_n-CH=CH_2$, in which $n = 0, 1,$ and 2 , shows the effect of conjugation ($n = 0$) on the value of $-\Delta H$, lowering it by about 3.5 Cal., an amount, it may be noted in passing, no greater than that produced by the introduction of two alkyl groups into ethylene. For many purposes of the *organic chemist*, however, it is more convenient to convert the results of sections B, C, and D of table 1 into the value of ΔH for the addition of only *one* mole of hydrogen. The results are then directly comparable with each other and with those in section A of table 1. The method of calculating the value of ΔH for the addition of the first pair of hydrogen atoms is, of course, very simple where the expected product (a substituted ethylene) has already been examined. For example, the addition of H_2 to allene

¹ The two isomeric octenes which have been examined yielded rather surprising results which, if their purity can be relied upon, indicate divergencies from the rules for more simple hydrocarbons. 2,4,4-Trimethylpentene-1 gave a value of 27.2 as compared with 28.4 for isobutene. But since the neopentyl group by itself was more effective in lowering $-\Delta H$ than any of the other alkyl groups tried, this discrepancy is not serious. The other compound, 2,4,4-trimethylpentene-2, with 28.4 Cal., is completely out of line.

would yield propylene and, since $-\Delta H$ of hydrogenation for propylene is 30.1, $-\Delta H$ for the reaction allene + $H_2 \rightarrow$ propylene is $71.3 - 30.1 = 41.2$. In the cases where the first product of the stepwise hydrogenation has not been hydrogenated in this laboratory, the value of ΔH can be estimated from general rules developed for section A of table 1. Such cases are noted by an asterisk in table 2, where the value of ΔH for the addition of one mole of hydrogen is given for the compounds listed in sections B, C, and D of table 1.

As table 2 illustrates, the open-chain conjugated systems give different calculated values of ΔH for the addition of one mole of hydrogen depending on the mode of addition; the greatest amount of heat is liberated if the addition is in the 1,4-position. If one takes this maximum value of $-\Delta H$ as a measure of the unsaturation of the system, then it is clear that butadiene-1,3 has a higher affinity for hydrogen than all compounds of the type $R_2C=CH_2$ or $RCH=CHR$ and only about 1 Cal. less than compounds of the type $RCH=CH_2$. The substitution of a methyl group on the end of the chain has diminished the maximum value by 3 Cal., an effect somewhat larger than that caused by the substitution of a methyl group in ethylene (2.7). Butadiene-1,3 is, as it were, the ethylene of the conjugated series. If this is the case the disubstituted derivative $CH_3CH=CH-CH=CHCH_3$ might be expected to differ from the parent compound by the same order of magnitude as $RCH=CHR$ from $CH_2=CH_2$. If this is so, the maximum value of ΔH for one mole of H_2 for $CH_3CH=CH-CH=CHCH_3$ would be about $-(+29.5 - 4.5) = -25.0$ Cal.; this estimated value is not far from that for cyclohexadiene (-26.8) but is clearly uncertain by several tenths of a Calorie. We would seem to be safe in taking the value of cyclohexadiene as typical of the terminally disubstituted butadienes. This is confirmed by the values obtained with two substituted cyclohexadienes, α -phellandrene and α -terpinene, although in both cases high purity can not be guaranteed. α -Phellandrene is the methylisopropylcyclohexadiene (I). The calculated value of $-\Delta H$,



using cyclohexadiene and the rules of aliphatic substitution, is $55.4 - 1.8 = 53.6$, in excellent agreement with the observed value 53.4. α -Terpinene

TABLE 2
 Calculated values of ΔH (355°K.) of hydrogenation by one mole of hydrogen





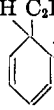


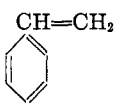
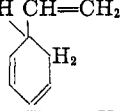
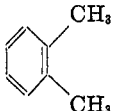
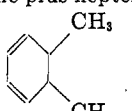
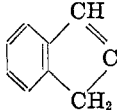
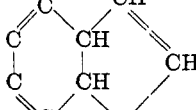
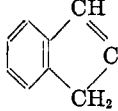
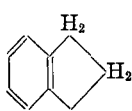
| COMPOUND HYDROGENATED | MODE OF ADDITION | PRODUCT | ΔH (355°K.) 1 MOLE OF H ₂ |
|---|-------------------|---|---|
| CH ₂ =C=CH ₂ | | CH ₃ CH=CH ₂ | -41.2 |
| CH ₂ =CH-CH=CH ₂ | 1,4 | CH ₃ CH=CHCH ₃ (<i>cis</i>) | -28.5 |
| CH ₂ =CH-CH=CH ₂ | 1,4 | CH ₃ CH=CHCH ₃ (<i>trans</i>) | -29.5 |
| CH ₂ =CH-CH=CH ₂ | 1,2 | CH ₃ CH ₂ CH=CH ₂ | -26.8 |
| CH ₂ =C-C=CH ₂ | 1,4 | (CH ₃) ₂ C=C(CH ₃) ₂ | -27.3 |
| $\begin{array}{c} \text{CH}_3 \quad \text{CH}_3 \\ \quad \\ \text{CH}_2 = \text{C} - \text{C} = \text{CH}_2 \end{array}$ | 1,2 | (CH ₃) ₂ CHC=CH ₂ | -25.9 |
| $\begin{array}{c} \text{CH}_3 \quad \text{CH}_3 \\ \quad \\ \text{CH}_3\text{CH} = \text{CH} - \text{CH} = \text{CH}_2 \end{array}$ | 1,4 | CH ₃ CH ₂ CH=CHCH ₃ (<i>cis</i>) | -25.5* |
| $\begin{array}{c} \text{CH}_3 \quad \text{CH}_3 \\ \quad \\ \text{CH}_3\text{CH} = \text{CH} - \text{CH} = \text{CH}_2 \end{array}$ | 1,4 | CH ₃ CH ₂ CH=CHCH ₃ (<i>trans</i>) | -26.5* |
| $\begin{array}{c} \text{CH}_3 \quad \text{CH}_3 \\ \quad \\ \text{CH}_3\text{CH} = \text{CH} - \text{CH} = \text{CH}_2 \end{array}$ | 1,2 | CH ₃ CH=CHCH ₂ CH ₃ (<i>cis</i>) | -25.5* |
| $\begin{array}{c} \text{CH}_3 \quad \text{CH}_3 \\ \quad \\ \text{CH}_3\text{CH} = \text{CH} - \text{CH} = \text{CH}_2 \end{array}$ | 1,2 | CH ₃ CH=CHCH ₂ CH ₃ (<i>trans</i>) | -26.5* |
| $\begin{array}{c} \text{CH}_3\text{CH} = \text{CH} - \text{CH} = \text{CH}_2 \\ \quad \\ \text{CH} = \text{CH} - \text{CH} = \text{CH} \end{array}$ | 3,4 | CH ₃ CH ₂ CH ₂ CH=CH ₂ | -23.8* |
| $\begin{array}{c} \text{CH}_3\text{CH} = \text{CH} - \text{CH} = \text{CH} \\ \quad \\ \text{CH}_2 - \text{CH}_2 \end{array}$ | 1,4 | CH ₂ CH=CHCH ₂ | -26.8 |
| $\begin{array}{c} \text{CH}_2 - \text{CH}_2 \\ \quad \\ \text{CH} = \text{CH} - \text{CH} = \text{CH} \end{array}$ | and 1,2 1,4 | CH ₂ —CH=CH—CH ₂ | -24.0 |
| $\begin{array}{c} \text{CH}_2 \\ \\ \text{CH} = \text{CH} - \text{CH} = \text{CH} \end{array}$ | and 1,2 1,4 | CH ₂ —CH=CH—CH ₂ | -8.0* |
| $\begin{array}{c} \text{O} \\ \\ \text{CH} = \text{CH} - \text{CH} = \text{CH} \end{array}$ | | (taking ΔH for this compound as for <i>cis</i> -butene-2) | |
| $\begin{array}{c} \text{CH} = \text{CH} - \text{CH} = \text{CH} \\ \quad \\ \text{O} \end{array}$ | 1,2 | CH ₂ -CH=CH | -11.5* |
| | | $\begin{array}{c} \text{CH}_2 - \text{O} \\ \quad \\ \text{CH}_2 - \text{CH} = \text{CH} \end{array}$ | |
| | | (taking ΔH for this compound as for 2-ethoxypropene) | |
|  | 1,4 |  | 7.4* |
| | | (estimated twice cyclohexene) | |
|  | 1,2 | Cyclohexadiene | 5.6 |
|  | 1,2 (ortho) |  | 6.5* |
|  | 1,2 (ortho) | | 5.9* |
|  | 1,4 | | 7.8* |
| C ₆ H ₅ CH=CH ₂ | | Ethylbenzene | -28.6 |

TABLE 2—Concluded

| COMPOUND HYDROGENATED | MODE OF ADDITION | PRODUCT | ΔH (355°K.) 1 MOLE OF H ₂ |
|---|------------------------|--|---|
|  | |  (assuming $\Delta H = \Delta H$ of cyclohexadiene plus heptene-1) | 7.9* |
|  | 1,2 (ortho) to give |  | 8.1* |
|  | 1,2 (ortho) to give |  | 12.4* |
|  | to give |  | -24.1 |
| Pentadiene-1,4 | 1,2 | CH ₃ (CH ₂) ₂ CH=CH ₂ | -30.7* |
| Hexadiene-1,5 | 1,2 | CH ₃ (CH ₂) ₃ CH=CH ₂ (taking heptene-1 value in both cases) | -30.4* |

is isomeric (II) and the calculated value is $55.4 - 2 \times 1.8 = 51.8$, as compared with 50.7.

The introduction of two methyl groups in the 2,3-position in butadiene-1,3 is striking. Comparing the maximum figures for 1,4-addition the difference is 2.2, while the corresponding difference for the 1,2-addition is only 0.8 Cal. Again clearly, the 1,4-positions in butadiene are like the 1,2-positions in ethylene itself and the value of ΔH is a sensitive reflection of disturbances in the molecule produced by substitution.

The value of ΔH for one mole of hydrogen added to the unconjugated dienes is somewhat higher than the corresponding value for propylene (cf. table 1 (A) and table 2). The "exaltation" is 0.6 Cal. with the pentadiene and 0.3 Cal. with the hexadiene; this may represent the dying out with lengthening of the chain of the enormous increase evident in allene where the juxtaposition of the two double bonds has increased the affinity for hydrogen by about 11 Cal. If this is the case the affinity of butadiene

itself must be the resultant of such an increase in affinity due to the proximity of the two double linkages and what has now come to be known as the "resonance energy" of the conjugated system. From the point of view of the organic chemist it is perhaps advantageous to speak of the decreased affinity for hydrogen due to conjugation. On this basis it is clear that it is well to avoid the case of compounds with a terminal $C=CH_2$ where a proper basis of comparison seems difficult, and consider as typical the comparison of $RCH=CH-CH_2CH_2R$ and $RCH=CH-CH=CHR$. If this is done the decrease in affinity due to conjugation would appear to be in the neighborhood of 2 to 3 Cal.

When we turn to the cyclic compounds we approach the problem of so-called aromatic compounds. The unsaturation of cyclohexadiene (as measured by ΔH of hydrogenation) is, as far as we can at present estimate, very close to that of the corresponding open-chain compound and only some 2 Cal. less than an unconjugated diene. In cyclopentadiene we have a very appreciable decrease (4.5) of affinity as compared with cyclohexadiene, whereas a comparison of cyclopentene and cyclohexene shows a decrease of affinity in the former of *ca.* 1.7 Cal. To understand these facts one should remember that cyclopentane is, according to combustion data, under a strain of some 4 Cal., while cyclohexane is not. The lower heats of hydrogenation of the five-membered rings (more positive ΔH) mean formally that the strain is increased by opening their double bonds. Thus cyclopentadiene must have less strain than cyclopentene, and this in turn less strain than cyclopentane. This conclusion is arrived at by supposing that no strains exist in the six-membered systems, as otherwise only a conclusion relative to the behavior of the six-membered rings is possible. In any case, however, it is in crass disagreement with the tetrahedral valence theory of carbon, which would predict increasing strain in the five-membered ring as the single bonds are replaced by the double bonds. But further facts seem to support it quite conclusively. Thus ΔH of the 1,2 hydrogenation of dihydroindene (see table 2) is more positive (1.7 Cal.) than that of *o*-xylene and the 1,2 hydrogenation in the five-membered ring of indene is more positive than the suitably corrected heat of hydrogenation of the side chain in styrene and is actually equal to the 1,2 hydrogenation of cyclopentadiene. Reasoning again quite formally, we may say that converting the five-membered ring in indene and hydrindene to a completely saturated ring evolves less heat than would be calculated by analogy with compounds not containing a five-membered ring. It thus appears that the strain in five-membered rings increases with decreasing unsaturation. This is a most surprising result and merits further investigation.

The best method of studying this problem is by measuring the heats of

hydration of cyclic acid anhydrides and lactones; such work is now planned in this laboratory.

Recent results obtained by studying coupling reactions of hydroxy derivatives indicate a striking difference between *o*-xylene on the one hand and hydrindene on the other. Measurements of dipole moments (6) tend to confirm the evidence that there is some rather fundamental difference between these two closely related compounds. Our results are not in agreement with these findings. There is a difference of only a few Calories in heat evolved in the hydrogenation by one mole of hydrogen of these two compounds, and the difference is in the opposite direction from that predicted on the basis of "fixed bond formulae" derived from the coupling reactions.

CONCERNING THE CHEMICAL PROPERTIES OF AROMATIC COMPOUNDS

When we come to furane, in table 2, the decrease of ΔH is so large (about 16 Cal.) that clearly a special factor must be involved; when we reach benzene and its derivatives the decrease is of the order of magnitude of 31 Cal. and the sign of ΔH has become reversed. From the point of view of the chemist the value of ΔF^0 is of more practical consequence than the value of ΔH . When ΔF^0 is equal to about -5 Cal., a gaseous reaction of type $A + B = C$ at one atmosphere pressure proceeds to a point where 1 per cent of the reactants exists at equilibrium; when $\Delta F^0 = 3$ Cal., only 1 per cent of the product is present at equilibrium. Thus if ΔF^0 is more positive than about $+3$, the reaction will apparently "not proceed" under usual conditions of pressure.

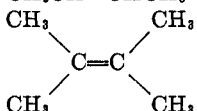
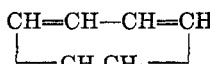
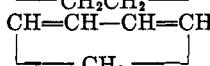
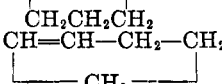
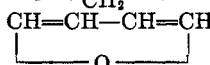
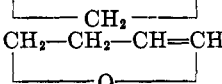
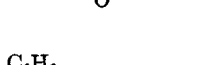
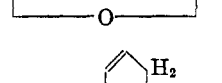

The values of ΔF^0 for the addition of one mole of hydrogen at 298°K. for some typical unsaturated compounds are given in table 3; the values of ΔH at 355°K. are taken from tables 1 and 2, reduced to 298°, and ΔS^0 estimated from the best data available.

An inspection of table 3 shows that although the free energy change attendant on the addition of one mole of hydrogen to many alkyl derivatives of ethylene and to butadiene and the cyclic dienes is a great deal less than for ethylene itself, the reactions will all run to practical completion. Quite different is the case of benzene; here the sign is reversed and $\Delta F^0 = +13.6$ Cal.; the amount of product in equilibrium with the reactants is negligible. It is impossible to form cyclohexadiene from benzene directly, not because of any question of relative rates of reactions but because of the energy change involved in the addition of one mole of hydrogen to the aromatic compound. With furane a measurable equilibrium should exist if the second step could be suppressed, whereas even the small value of -14.8 for cyclopentadiene is ample to ensure complete reaction with one mole of hydrogen. Towards hydrogen and a catalyst furane and

benzene are quite different in their behavior from the other unsaturated compounds; with them it is hopeless to attempt to add one pair of hydrogen atoms to the unsaturated system.

The peculiar chemical properties of benzene and its derivatives which first attracted the attention of organic chemists are clearly due to the fact that in these compounds the energy relationships are such that an addition reaction involving one double linkage (or its equivalent) will not proceed to any appreciable extent. Unfortunately, we cannot predict with any

TABLE 3
Values of ΔF^0 for the addition of one mole of hydrogen at 298°K. for some unsaturated hydrocarbons
(Gaseous state)

| COMPOUND | ADDENDUM | PRODUCT | 298°K. | | |
|---|--------------|---|------------|----------------|--------------|
| | | | ΔH | $-T\Delta S^0$ | ΔF^0 |
| $\text{CH}_2=\text{CH}_2$ | H_2 | C_2H_6 | -32.6 | 8.2 | -24.4 |
| $\text{CH}_3\text{CH}=\text{CH}_2$ | H_2 | $\text{CH}_3\text{CH}_2\text{CH}_3$ | -29.9 | 8.9 | -21.0 |
| $\text{CH}_3\text{CH}=\text{CHCH}_3$ (<i>cis</i>) | H_2 | $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$ | -28.2 | 8.9 | -19.4 |
|  | H_2 | $(\text{CH}_3)_2\text{CHCH}(\text{CH}_3)_2$ | -26.4 | 8.9 | -17.5 |
| $\text{C}_6\text{H}_5\text{CH}=\text{CH}_2$ | H_2 | $\text{C}_6\text{H}_5\text{CH}_2\text{CH}_3$ | -28.3 | 8.9 | -19.5 |
| $\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$ | H_2 | $\text{CH}_3\text{CH}=\text{CHCH}_3$ (<i>trans</i>) | -29.2 | 8.9 | -20.3 |
|  | H_2 | $\text{CH}=\text{CH}-\text{CH}_2$ | -26.5 | 8.8 | -17.7 |
|  | |  | -23.7 | 8.8 | -14.8 |
|  | H_2 |  | -11.4 | 8.9 | -2.5 |
|  | |  | | | |
| C_6H_6 | H_2 |  | 5.8 | 7.8 | 13.6 |

accuracy the energy changes which accompany the interaction of unsaturated compounds with such reagents as the halogens, halogen acids, and water (with acid as a catalyst); table 4 summarizes the data now available. If one may extrapolate from these few facts it seems extremely probable that for none of the common reagents is ΔF^0 more than a few Calories more negative than for hydrogen, while for many it is much more positive. This being the case we can easily understand why benzene and its derivatives are "not unsaturated" when tested with such reagents as bromine. No addition reaction involving one mole of reagent is possible

(ΔF^0 is too positive), and a simultaneous addition of two or three moles of the reagent is too difficult kinetically to occur at a measurable rate; this being the case other reactions such as substitution are possible, and proceed. Comparing styrene (phenylethylene) with propylene (table 3) we see the affinity of the former for H_2 (as measured by ΔF^0) is 1.4 Cal. less than that of the latter; if a similar difference holds for the tetrasubstituted compounds we may predict ΔF_{298}^0 (gaseous state) for the reaction $(C_6H_5)_2C=C(C_6H_5)_2 + H_2$ to be about -12.5 . (In solution this value may be decreased or increased by as much as 2 Cal.) Tetraphenylethylene thus approaches furane, and if the energy changes with other reagents parallel those with hydrogen we should predict that this compound will not combine with iodine (ΔF^0 being 22 Cal. more positive than with H_2) nor with hydrobromic acid (ΔF^0 perhaps 18 Cal. more positive than with H_2) or similar reagents, among which nitric and sulfuric acids may well be included. Until more accurate data are available for simple halogenations

TABLE 4
Addition reactions of ethylene in the gaseous state at 298°K.

| ADDENDA (GASES) | ΔH | $T\Delta S$ | ΔF | METHOD |
|--------------------|-------------|-------------|-------------|---------------------------|
| | <i>Cal.</i> | <i>Cal.</i> | <i>Cal.</i> | |
| H_2 | -32.6 | -8.2 | -24.4 | Direct ΔH |
| Cl_2 | -42 (?) | -12 (?) | -30 (?) | Heats of combustion |
| Br_2 | — | — | — | No data |
| I_2 | -13.6 | -11 | -2.2 | Direct K |
| H_2O | -10.8 | -8.3 | -2.5 | Heats of combustion and K |
| HBr | -18 (?) | -10 (?) | -8 (?) | Heats of combustion |

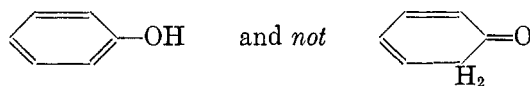
exact predictions are obviously dubious, but it is interesting to note that whereas diphenyl derivatives of ethylene combine with both chlorine and bromine, tetraphenylethylene reacts with chlorine to form a dichloride (5) but will not add bromine (1). This indicates that the free energy of addition of chlorine to a double bond is of similar magnitude to that of hydrogenation (cf. table 4) but the affinity of bromine is 10 to 15 Cal. less.

There thus emerges from a consideration of the energy changes involved in addition reactions of unsaturated compounds a clear picture of the peculiar properties of certain classes of unsaturated compounds which have been designated for generations as "aromatic." The affinity of these aromatic compounds for one mole of addendum is so small that no appreciable addition can take place quite irrespective of any considerations involving rates of reactions. This being so, other types of reactions such as substitution proceed instead of addition reactions. It is obvious, however, that there may be some compounds which will show "typical aromatic

properties" (i.e., no addition reactions involving *one* mole) when treated with certain reagents which have low affinity for the carbon-carbon double bond and yet will combine like other unsaturated compounds with other reagents. The organic chemist long ago ruled out iodine as a suitable reagent for distinguishing between aromatic and aliphatic unsaturated compounds, as it was known that this element would not combine with many simple double bonds. On the other hand, there is clear evidence that ozone will combine mole for mole even with benzene compounds. The qualitative behavior of a compound is thus clearly dependent on the reagent chosen, and if the reaction involving one mole proceeds it throws no light on whether ΔF^0 is just over the line for an essentially complete reaction or whether the free energy change is very large. The only reason for dwelling on these obvious points at such length is that in lieu of accurate quantitative data there is an almost irresistible temptation to argue from qualitative information. The much quoted cyclooctatetraene is a case in point. It is cited as being non-aromatic because it reacts with bromine, is oxidized by potassium permanganate, etc. All this might be true and yet the affinity of the compound might be essentially that of cyclohexadiene (ΔF^0 for one mole of hydrogen, -17.7) or significantly lower by as much as 15 Cal. (if bromine and hydrogen have the same order of affinity for unsaturated compounds). Many theoretical arguments have been based on the non-aromatic nature of cyclooctatetraene. Clearly until one has quantitative data in regard to the energy changes involved when cyclooctatetraene combines with hydrogen (or some other reagent) one is on uncertain ground. The most that can be argued from the qualitative information is that its affinity for an addendum is not as low as in the case of benzene.

PHENOLS AND ENOLS

In addition to the chemical peculiarities of the parent hydrocarbons, aromatic compounds are also characterized by the fact that the unsaturated hydroxy compounds are stable in the enol form. Thus C_6H_6O is predominantly if not exclusively

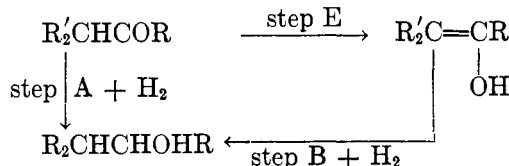


whereas C_2H_4O is $\begin{array}{c} \text{CH}_3\text{C}=\text{O} \\ | \\ \text{H} \end{array}$ and not $\begin{array}{c} \text{CH}_2=\text{C}-\text{OH} \\ | \\ \text{H} \end{array}$. The relation between this property and the lowered affinity of the unsaturated system is at once apparent from the following considerations: Consider the com-

pound $R_2'CHCOR$ and its enol $R_2'C=CR$, where R and R' may be of any

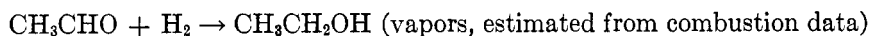


nature including parts of the same cyclic system. The reduction to $R_2'CHCHOHR$ may proceed as follows in one of two ways:

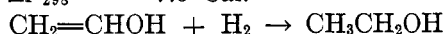


The free energy change (ΔF^0) of the reduction step A is obviously equal to the sum of the free energy changes in the other two steps. Thus ΔF^0 (enolization) = ΔF^0 (reduction of carbonyl compound) - ΔF^0 (reduction of enol). The first term on the right-hand side of this equation is small (about -6) and probably only little affected by changes in structure. Therefore, as an approximation ΔF^0 (enolization) = 6 - ΔF^0 (of reduction of enol). The energy changes in the reduction of the enol will closely parallel those of the corresponding unsaturated hydrocarbon, except in cases where chelation occurs. Thus, corresponding to the low affinity of aromatic compounds for hydrogen, we find high stability of the enol (large negative values of ΔF^0 of enolization). The following rough estimates will serve as illustrations and also show how an approximate measure of the free energy of enolization of aliphatic ketones and aldehydes may be obtained.

For acetaldehyde



$$\Delta F_{293}^0 = -7.5 \text{ Cal.}$$



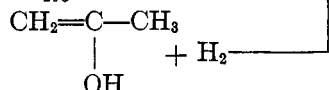
$$\Delta F_{293}^0 = -21.0 \text{ Cal. (estimated from } \Delta H_{355} \text{ as mean of } -31.1 \text{ from vinyl acetate and } -28.6 \text{ from } \frac{1}{2} \text{ divinyl ether} = -30.0)^2$$

$$\Delta F_{293}^0 \text{ (enolization)} = +13.5 \text{ (wholly ketonic)}$$

For acetone



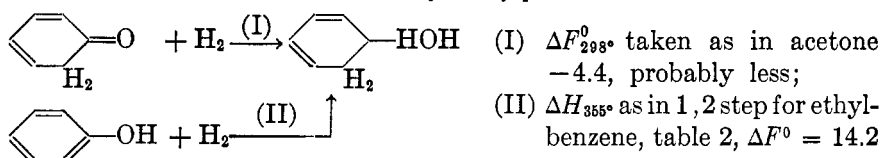
$$\Delta F_{293}^0 = -4.4$$



² Since this paper was set in type, the heat of hydrogenation of ethyl vinyl ether has been measured and found to be -26.7 Calories. This lowers the value ΔF_{293}^0 for $CH_2=CHOH + H_2 \rightarrow CH_3CH_2OH$ to -17.9 Calories and ΔF_{293}^0 (enolization) = +10.4 Calories.

ΔF_{298}^0 (estimated from $\Delta H_{355} = -25.1$ for 2-ethoxypropene) = -16.3
 ΔF_{298}^0 (enolization) = $+11.9$ (wholly ketonic). This value confirms the very approximate estimate of $\Delta F^0 = 10$ to 12 Cal. made by Conant and Carlson (2) from the activation energies of enolization as measured by the temperature coefficient of the rate of racemization of certain ketones.

For the keto form of phenol



ΔF_{298}^0 (enolization) = -18.6 (wholly enolic)

For the hydroxy derivatives of furane (only known in the case of complex derivatives) one can estimate ΔF^0 (enolization of the keto form) of approximately $-6.7 - (-2.5) = -4.2$ or $K = 10^{-3}$, essentially wholly enolic. If the combustion data for naphthalene and its hydrogenation products can be relied on, the unsaturation of the dicyclic system (in terms of ΔF^0 for one mole of hydrogen) is a few Calories less than that of furane; one would thus predict that the hydroxyl derivatives of naphthalene would be stable in the enolic form as, of course, they are. For a measurable equilibrium between the keto and enol forms, ΔF^0 (of enolization) should lie between about -3 and $+3$ and this in turn would mean a value of ΔF^0 of hydrogenation of the parent hydrocarbon of -9 to -3 (the corresponding ΔH values being about -18 and -12). The phenylated ethylenes approach this range, and it is therefore not surprising that although modern work has shown that triphenylvinyl alcohol, $(\text{C}_6\text{H}_5)_2\text{C}=\text{COHC}_6\text{H}_5$, is in reality wholly the ketonic form, $(\text{C}_6\text{H}_5)_2\text{CHCOC}_6\text{H}_5$, nevertheless the compound so readily forms enolic derivatives that it was long regarded as enolic. The corresponding mono-phenyl and diphenyl derivatives do not show the same behavior.

The equilibrium between anthrone and anthranol in alcoholic solution is such that 80 per cent of the keto form is present (4). From this we may estimate that the value of ΔH for hydrogenation of anthracene at the 9,10-position is approximately -15 Cal., since the ΔF^0 of the tautomerization of the 9-hydroxyl derivative is about zero. This prediction we hope to test shortly by direct calorimetric measurements. If it is confirmed, it will place this addition reaction of anthracene between those of furane and cyclopentadiene, which is in accord with the fact that anthracene forms

a dibromide addition product when treated with bromine. Too few carbonyl compounds have been measured as yet to make it worth while to do more than draw attention to the rôle of the oxygen atom in influencing the affinity of the double bond. Judging from divinyl ether, methoxypropene, and crotonaldehyde, both the carbonyl and the *oxygen* of an ether linkage are capable of conjugation with neighboring double bonds; thus divinyl ether is approximately the equivalent of $\text{CH}_2=\text{CH}-\text{CH}=\text{CH}-\text{CH}=\text{CH}_2$. The quantitative measure of their action is about the same as for a carbon-carbon double bond, but an exception is found in vinyl acetate, for which a larger ΔH value has been found than calculated even without conjugation. The decision as to whether this is generally connected with the second oxygen atom of the carboxyl group must await further work.

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