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Heats of Organic Reactions. VIII. Some Further Hydrogenations, Including Those of Some Acetylenes

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In the previous publications of this series¹ have been reported the heats of addition of hydrogen to a wide variety of unsaturated organic molecules as well as the heats of addition of chlorine and bromine to some of the simpler ethylenic hydrocarbons. The data previously presented have shown correlation between molecular constitution and the thermal effects accompanying these addition reactions. The generalizations drawn and semi-empirical rules formulated have been amplified and modified as the progress of the investigation justified. In the present paper we shall present some additional data, and, it being essentially the final report on this work, we shall give a discussion of the entire set of data from a concordant point of view. The information of general significance which emerges from it concerns the rather strong interactions between non-bonded atoms or atomic groups within a molecule.

Preparation of Materials

We are indebted to the late Professor E. P. Kohler and his co-workers for the cyclic compounds used in this work; their preparation is reported elsewhere.²

Acetylene.—Tank acetylene (Prest-O-Lite) was purified by passage through a series of 10 spiral wash bottles, which contained in order: (1) saturated sodium bisulfite solution, (2) water, (3) and (4) 0.2 *N* iodine in aqueous potassium iodide solution, (5) and (6) sodium thiosulfate solution, (7) and (8) alkaline sodium hydrosulfite with sodium anthraquinone β -sulfonate as indicator and oxygen carrier, (9) and (10) 10% aqueous potassium hydroxide solution. The gas then traversed a trap in Dry-Ice and two large drying tubes, the first of which contained calcium chloride and the second, Dehydrite. A 38-cm. mercury escape valve served to ensure a constant back pressure. The solutions described above were renewed just prior to each run and never became exhausted during their period of use.³

Methylacetylene.—Sodium acetylide was prepared by passing acetylene, purified as above, into a Dry-Ice cooled solution of 72 g. of sodium in 1 l. of liquid ammonia until the blue color disappeared.

Methyl sulfate (400 g.) which had been washed previously with sodium bicarbonate solution and dried with anhydrous magnesium sulfate was next introduced by means of a special dropping funnel, so designed as to de-

liver small droplets, and containing a side-arm on both the stem and the pressure equalizer tube through which a slow stream of nitrogen passed. This device protected the tip and the liquid in the funnel from contact with ammonia. It had been found previously that an ordinary funnel not only delivered drops of such size as to cause an almost explosive reaction, but also soon became plugged with a white solid (presumably $\text{CH}_3\text{NH}_3\text{SO}_4\text{CH}_3$).

When introduction of methyl sulfate was started the bath was allowed to warm up to the boiling point of the ammonia. The exit gases were freed from ammonia by passage through 2.5 liters of water and 1.5 liters of 12 *N* sulfuric acid. The latter solution never became alkaline. The hydrocarbon was dried with a large calcium chloride tower and then condensed in a trap immersed in Dry-Ice-methanol mixture. The yield of crude methylacetylene was 83%, in agreement with the observation of Vaughn, Hennion, Vogt and Nieuwland.⁴

The product was given a double bulb-to-bulb distillation to free it as well as possible from acetylene, and then fractionated in a six-foot (1.8-meter) vacuum-jacketed Podbielniak type column. The middle fraction, which boiled at $-23.23 \pm 0.05^\circ$ (760 mm.) was transferred *in vacuo* to a small monel metal tank just before use. The freezing point was -102.74° .⁶

Dimethylacetylene.—Initial attempts to prepare this hydrocarbon from sodium methylacetylide and methyl sulfate gave unsatisfactory yields: however, the dialkyl acetylene synthesis described by Bried and Hennion⁷ was found to work very well. Sodium acetylide was prepared in the usual manner from 25 g. of sodium in 500 cc. of liquid ammonia, and to this a suspension of sodamide from 30 g. of sodium in 500 cc. of liquid ammonia⁸ was added, followed by 266 g. of methyl sulfate with stirring. After standing overnight at -80° , the contents of the flask were boiled off; the ammonia was removed as before, and the hydrocarbon was condensed in a series of two traps, the first of which was kept at -20° , and the second at -80° . Nearly all of the dimethylacetylene was caught in the first trap. The yield of crude product was 80%. The hydrocarbon was fractionated in the six-foot Podbielniak column; the portion reserved for calorimetric study boiled at $26.69 \pm 0.03^\circ$ (760 mm.).⁹

Dimethyldiacetylene.—Methylacetylene was generated from purified propylene bromide and potassium hydroxide in boiling butyl alcohol according to Heisig and Davis.⁹ The yield was 81%.

(4) Vaughn, Hennion, Vogt and Nieuwland, *J. Org. Chem.*, **2**, 1 (1937).

(5) Heisig and Hurd, *THIS JOURNAL*, **55**, 3845 (1933), give the boiling point of methylacetylene as -23° from vapor pressure data.

(6) Maass and Wright, *ibid.*, **43**, 1098 (1921), give f. p. -104.7° .

(7) Bried and Hennion, *ibid.*, **59**, 1310 (1937).

(8) Vaughn, Vogt and Nieuwland, *ibid.*, **56**, 2120 (1934).

(9) Heisig and Davis, *ibid.*, **57**, 339 (1935), give 27.2° as the boiling point.

(1) *THIS JOURNAL*, **57**, 65 (1935); **57**, 876 (1935); **58**, 137 (1936); **58**, 146 (1936); **59**, 831 (1937); **60**, 440 (1938); **60**, 2764 (1938). These are referred to hereinafter as I to VII.

(2) Kohler, Tishler, Thompson and Potter, *ibid.*, **61**, 1057 (1939).

(3) We are indebted to Dr. F. B. Downing of E. I. du Pont de Nemours and Co. for suggesting this system to us.

TABLE I
 HYDROGENATION OF CYCLIC HYDROCARBONS

Compound	B. p. (760 mm.), °C.	Reactant n_{20}^D	Product, n_{20}^D	Expts. made	Reaction, $-\Delta H_{365}$, cal./mole	Estimated over-all accuracy
C_7H_{12}	114.35 \pm 0.03 ^a	1.4580 ^b	1.4449 \pm 0.0001 ^d	2	26,515 \pm 20	150
C_7H_{10}	121.52 \pm .01 ^a	1.4991	1.4449 \pm .0001 ^d	3	51,260 \pm 49	150
C_7H_8	115.55 \pm .05 ^a	1.5213	1.4449 \pm .0001 ^d	2	72,846 \pm 10	300
C_8H_{14}	144.52 \pm .01 ^a	1.4702 ^c	1.4583 \pm .0001 ^e	3	23,525 \pm 35	150

^a Willstätter, *Ann.*, **317**, 219 (1901), reports b. p. (724 mm.) 115° for cycloheptene, b. p. (724 mm.) 120–121° for cycloheptadiene, and b. p. (724 mm.) 116° for cycloheptatriene. ^b Rosanov, *J. Russ. Phys.-Chem. Soc.*, **48**, 317 (1916), reports n_{20}^D 1.4552. ^c Willstätter and Waser, *Ber.*, **43**, 1180 (1910), report b. p. (730 mm.) 145° and n_{20}^D 1.474 for cyclooctene and n_{20}^D 1.4586 for cyclooctane. ^d Reference *b* reports n_{20}^D 1.4440 for cycloheptane.

The methylacetylene was now converted to the cuprous salt by passing it slowly into a vigorously stirred solution of 1.5 times the theoretical amount of ammoniacal cuprous chloride. Absorption was complete. The cuprous methylacetylde was filtered off and preserved in a desiccator containing concentrated ammonia water.

When an attempt was made to oxidize all of the cuprous salt by once with potassium ferricyanide as described by Griner,¹⁰ much methylacetylene was regenerated and very little of the desired product was obtained. However, when the salt was added in small portions to the hot, rapidly stirred ferricyanide solution, the yield was 42%. The hydrocarbon sublimed cleanly with steam from the reaction flask and was washed with distilled water and dried over Dehydrite. It developed a slight yellow tinge on long standing, but could be freed from this impurity by subliming with steam.

Results

Cyclic Hydrocarbons.—Incompleteness of reaction was tested for by the usual bromine (II) titration. In no case was unsaturation found in the product. There was no irreversible adsorption on the cobalt-nickel catalyst and a large variation of relative rates of flow of hydrogen and hydrocarbon had no effect on the heat evolved. As Kohler, Tishler, Thompson and Potter² have indicated, it is very difficult to obtain these hydrocarbons in a pure state as judged by the freezing point method. The difficulty of their preparation in general precludes the use of Column A for their distillation, and repeated fractionations through Column B failed to give a product with a flat freezing curve. Two reasons lead us to believe that this failure is not serious. The first is the extremely large freezing point depression constants which uniformly characterize these hydrocarbons. Thus even a minute amount of impurity would give the material a poor freezing point. The second is a result of repeated hydrogenations of cycloheptene using samples of different purities as judged by the freezing points. Three different samples were used which gave samples of cyclo-

heptane freezing at -12.2° , -8.4° and -8.4° .¹¹ However, the heat of hydrogenation of the entire set can be expressed as $26,419 \pm 56$ cal. per mole. The average of the two runs with cycloheptene which had been distilled through column A is about 100 cal. higher than this average and represents what we consider the correct value. The earlier results are quoted only to show how much more sensitive the freezing point test is than the heat of the reaction. The cycloheptene itself tended to form a glass and it was difficult to get good freezing curves. The best sample froze at about -56° .

The cycloheptadiene gave a good freezing flat at -110.4° . The product of hydrogenation gave an excellent flat at -7.98° . This we take to be the true freezing point of cycloheptane.

Cycloheptatriene gave only a fair "flat" at -79.5° , and its hydrogenation product froze at -8.3° .

The cyclooctene froze at -22.1° and the hydrogenation product froze at 7.95° . Both of these determinations left much to be desired as freezing points but do not indicate any large amounts of impurities. Table I shows the pertinent data on these compounds.

Cyclic Ketones.—The hydrogenation of the cyclic ketones proceeded smoothly on the cobalt-nickel catalyst. There was no irreversible adsorption, and variations in the rates of flow produced no effect. As was the case with acetone and methyl ethyl ketone, the hydrogenation was not complete. This incompleteness was measured in the following manner: 0.5 cc. of the product was mixed with an equal volume of sodium methoxide and 1 cc. of a standard solution of *p*-nitrobenzaldehyde in methyl alcohol. After heating gently for two minutes the color was matched with that produced by a 0.5% solution of the ke-

(10) Griner, *Ann. chim.*, [6] **26**, 354 (1892).

(11) Willstätter and Kametaka, *Ber.*, **41**, 1481 (1908), report -12 to -13° .

TABLE II
 HYDROGENATION OF CYCLIC KETONES

Compound	B. p., °C.	Mm.	Reactant		n_D^{20}	F. p., °C.	Product	n_D^{20}
			F. p., °C.					
C_5H_8O	131.15	774 ^a	-51.64 ^b		1.4370 ^a	1.4535	$\pm 0.0005^c$
$C_6H_{10}O$	155.47	767 ^a	-29.05		1.4512 ^c	20.99 ^d	1.4667	$\pm .0001$

Compound	Expts. made	Reaction, $-\Delta H_{315}$ meas.	% incomplete	$-\Delta H_{315}$ corr.	Estimated over-all accuracy
C_5H_8O	3	12,374 \pm 61	0.9	12,498 \pm 61	150
$C_6H_{10}O$	3	15,317 \pm 81	.7	15,424 \pm 81	150

^a Beilstein gives b. p. 155.4° for cyclohexanone; for cyclopentanone, b. p. 130.0–130.5°. ^b Timmermans, *Bull. soc. chim. Belg.*, **36**, 502 (1922), gives f. p. -52.8°. ^c Landolt-Börnstein gives n_D^{20} 1.4507. ^d Lange, *Z. physik. Chem.*, **A161**, 77 (1933), gives f. p. 25.47°. ^e Noller and Adams, *THIS JOURNAL*, **48**, 1084 (1926), give n_D^{20} 1.4530.

tone in methyl alcohol, by diluting the unknown with methyl alcohol until a match was obtained. This test consistently showed a concentration of 0.9% of ketone in the case of the cyclopentanone and 0.7% in the case of the cyclohexanone. No trace of dimolecular reduction could be detected by carefully fractionating samples of the product in a small Podbielniak still.

A calculation of the incompleteness of the hydrogenation from the freezing point of the product in the case of the cyclohexanone yields a figure in substantial agreement with that found by means of the above test. The true freezing point of cyclohexanol was used as 25.47° and the freezing point depression constant was taken from "I. C. T." Table II lists the pertinent data on these compounds.

Acetylenic Compounds.—Acetylene and methylacetylene were hydrogenated over a 10% platinum on asbestos catalyst. In neither case could any irreversible adsorption be detected. Wide variations in the rate of gas flows failed to show any effect on the heat produced. Ammoniacal silver nitrate solution was used to test for 1-acetylenes in the product; the exit gases were passed through the reagent for five minutes. In every case this test was negative. Samples of the ethane and propane from the hydrogenations were collected and subjected to vapor pressure measurements in a differential manometer. No significant differences in vapor pressure between the first and last fractions to vaporize could be detected. Thus polymers were shown to be absent. Dimethylacetylene would not hydrogenate completely over the 10% platinum catalyst, and therefore the reaction was carried out on cobalt-nickel, at 82°. A bromine titration test showed only 0.01% unsaturation in the hydrogenation product, but the irreversible adsorption test was somewhat inconclusive. There may have been

a small amount of condensation on the catalyst, which also was manifested by a slight progressive change in the heat liberated with the repetition of the measurements. We believe that the true heat of reaction is slightly higher than reported and are increasing the estimate of the over-all error to care for this possibility. An attempt was made to hydrogenate dimethyldiacetylene but due to an incomplete reaction on the platinum catalyst and considerable irreversible adsorption on cobalt-nickel the effort was unsuccessful. Table III gives the data on these compounds.

 TABLE III
 HYDROGENATION OF ACETYLENES

Compound	Expts. made	$-\Delta H_{315}$	Estimated over-all accuracy
C_2H_2	3	75,062 \pm 66	150
$CH_3C\equiv CH$	3	69,703 \pm 14	150
$CH_3C\equiv CCH_3$	3	65,581 \pm 130	300

Discussion

1. **The New Experimental Data.**—Rather large variations of the heats of hydrogenation in the cycloolefin series are reported here and in the preceding papers (III and V). The numerical values, which range from 28.59 kcal. for cyclohexene to 23.52 kcal. for cyclooctene, are spread over almost as wide a range as those observed in the ethylene (32.82 kcal.) to tetramethylethylene (26.63 kcal.) series, although in the present case a constant number of alkyl groups are adjacent to the double bond. The following discussion will make plausible the contention that the same fundamental cause is responsible for the variations of the reaction heats in both series of compounds, namely, the interactions of the newly formed bonds with near-by, non-bonded atoms and atomic groups.

Hydrogenation of rings with increased unsaturation has provided information on the resonance energy in these conjugated systems. If, in ac-

TABLE IV
EFFECT OF SUBSTITUENTS ON THE HEATS OF HYDROGENATION

Reaction	ΔH_{ass} , kcal.	Diff.	Reaction	ΔH_{ass} , kcal.	Diff.
$\text{C}_2\text{H}_2 + \text{H}_2$	-42.24		$\text{C}_2\text{H}_4 + \text{H}_2$	-32.82	
$\text{CH}_3\text{C}\equiv\text{CH} + \text{H}_2$	-39.59	2.65	$\text{CH}_3\text{CH}=\text{CH}_2 + \text{H}_2$	-30.11	2.71
$\text{CH}_3\text{C}\equiv\text{CCH}_3 + \text{H}_2$	-37.63 ^a	1.96	$\text{CH}_3\text{CH}=\text{CHCH}_3 + \text{H}_2$	-27.95 ^a	2.16

^a To and from an equilibrium mixture of *cis*- and *trans*-butenes-2.

cordance with the procedure used in earlier papers of this series, the resonance energy in a diene is taken as the difference in the heats of hydrogenation of the diene to an olefin and of this olefin to the paraffin, then cycloheptadiene has 2.77 kcal. resonance energy. Comparison with cyclohexadiene (1.81 kcal.) and cyclopentadiene (2.96 kcal.) shows that it is substantially the same in all ring compounds, but is somewhat smaller than in the open chain dienes (3 to 4 kcal., *cf.* V). It should be noted, however, that the steric effects discussed later make the calculation of the resonance energy in all these instances somewhat doubtful.

A subtraction of the heat of hydrogenation of cycloheptatriene from that of cycloheptene, taken three times, leaves 6.7 kcal. as the resonance energy in the former. Steric effects again make the absolute magnitude of this value somewhat uncertain, but they should be substantially eliminated by taking the ratio of the resonance energies of cycloheptatriene and diene. This is found equal to 2.4, while Pauling and Sherman and later Lennard-Jones¹² calculated for open chain trienes and dienes the ratio 2.1.

The heats of hydrogenation of cyclic ketones are of some interest because they reproduce the trend established for cycloolefins, the six-membered ring compound having again the higher heat of reaction. In the present case, however, it is cyclopentanone which has a reaction heat (12.50 kcal.) close to that of its open chain homologs (13.34 and 13.17 kcal. for acetone and methyl ethyl ketone, respectively, *cf.* VI), while the heat evolution with cyclohexanone is almost as large as with acetaldehyde (15.42 and 16.75 kcal., respectively).

The heats of hydrogenation of acetylene and its homologs vary with substitution of alkyl groups in much the same manner as do those of ethylene and its homologs. The analogy between the two series of compounds is even quantitative, as the following Table IV shows. This constitutes additional evidence for the conclusion reached (VII) on the basis of the heats of bromination of olefins,

(12) Pauling and Sherman, *J. Chem. Phys.*, **1**, 879 (1933); Lennard-Jones, *Proc. Roy. Soc. (London)*, **A158**, 280 (1937).

that the variations in the heats of addition reactions are caused mainly by the steric effect of substituents on the addenda used in the reactions. Were the effects of substituents on the several carbon-carbon bonds involved in hydrogenations considerable, the result of Table IV would be a rather improbable accident.

The following discussion is an effort to evaluate the character and magnitude of these effects.

2. The General Nature of Steric Effects.—Of all the available data the heats of hydrogenation of unsaturated ring compounds supply perhaps the most direct, although qualitative, information on the character of interactions of non-bonded atoms within a molecule. In a paper of this series (V) comments were made on the heats of hydrogenation of five-membered rings which, being some 2 kcal. lower than those of corresponding six-membered systems and of open chain disubstituted ethylenes, seemed to disprove the existence of strain energy in cyclopentene and cyclopentadiene although the bond angles in these compounds deviate from tetrahedral values. In the meantime Professor Pauling has told one of the present authors that in the opinion of Dr. V. Schomaker this conclusion is subject to revision because five-carbon systems are planar, while six-carbon rings are puckered. In the planar rings the C-H bonds must be in the eclipsed configuration, while in puckered rings they may take up staggered positions; hence the relative heats of hydrogenation may be employed to evaluate the strain energy in cyclopentene only after correction has been made for these steric effects. Studies of the internal rotation of methyl groups in ethane¹³ have indeed shown that approximately 2.75 kcal. energy difference exists between the staggered and the eclipsed (in-line) configuration of the C-H bonds in the two methyl groups.

Two alternatives must now be considered, both of which are consistent with the observations on ethane: the configuration of lowest energy may be that in which C-H bonds are farthest apart

(13) See Kistiakowsky, Lacher and Stitt, *J. Chem. Phys.*, **7**, 289 (1939), for other references.

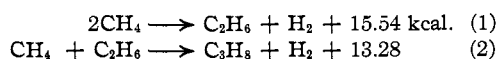
(staggered) or that in which they are closest together. If the former is true, then the low heats of hydrogenation of cyclopentene and pentadiene are due to the placement of hydrogen atoms into positions of higher energy as compared with the reaction of cyclohexene and a correction for this effect will result in values at least qualitatively consistent with the expected strain energies of the unsaturated C_5 rings. But if this explanation is the correct one, then the heat of combustion of cyclopentane, per CH_2 group, should be larger than that in open chain paraffins by about 3 kcal. because in the former the carbon bonds are not free to take up the (staggered) positions of lowest energy. Experimental data¹⁴ give 157.9 kcal. (Swietoslawski) heat of combustion per CH_2 group in cyclopentane and 157.5 kcal. (Swietoslawski) in methylcyclopentane as against 157.9 kcal. (Richards) or 157.2 kcal. (Swietoslawski) in cyclohexane and 157.1 (Rossini) in normal open chain hydrocarbons, all referred to the vapor phase. These data suggest about 0.5 kcal. excess energy content per CH_2 group in cyclopentane and are in poor agreement with the discussed interpretation (the uncertainties are, however, large). Nevertheless, the other alternative leads to much greater inconsistencies. Cyclohexane, in which, due to puckering, the C-H bonds cannot all have in-line configuration, has nearly the same heat of combustion per CH_2 group as the open chain hydrocarbons, instead of being considerably higher. Furthermore, the lower heats of hydrogenation of the C_5 rings now must mean that the strain energy decreases with increasing unsaturation (*i. e.*, with increasing deviation from tetrahedral angles!), becoming negative unless the experimental heat of combustion of cyclopentane is in error by being too low. In this case, however, large strain energy would have to be assigned to cyclopentane, even though the C-C-C angles in this compound (108°) barely deviate from tetrahedral values. All this is so improbable that we select the first alternative unreservedly and assume that the positions of minimum energy are those in which the C-H bonds are farthest apart, *i. e.*, the staggered configuration of ethane.

The greater stability of the staggered configuration of C-H bonds may be formally ascribed to the existence of repulsive interactions ("steric hindrance") between non-bonded atoms in poly-

atomic molecules. The observed lower heats of hydrogenation of rings larger than cyclohexene are consistent with this idea since hydrogen atoms on non-adjacent carbons are forced close together in such rings because of their extensive puckering. Further supporting evidence is offered by the observations that the energy content difference of *cis*- and *trans*-butenes-2 is 0.95 kcal.¹⁵ at $355^\circ K$. The planar zig-zag hydrocarbon chains in crystals also speak for the staggered configuration being the stable one. It appears¹⁶ that the heats of fusion of the normal hydrocarbons are substantially higher than those of corresponding cyclo-paraffins. Supposing that the staggered configuration of the crystalline straight chain compounds were the strained one, the opposite relation could be expected. Still other favorable facts will be cited in the following.

3. The Relative Energies of Steric Hindrance.—The repulsive interactions in polyatomic molecules result in inconstancy of bond energies. However, whichever one speaks of, one is beset by a rather fundamental difficulty in stating a precise experimental definition of the magnitude of the interaction energy or of the variable bond strength. Consider, for instance, the two hypothetical reactions: $CH_4 \rightarrow CH_3 + H + E_1$ and $C_2H_6 \rightarrow C_2H_5 + H + E_2$. The difference $E_2 - E_1$ may be taken as the direct measure of the difference in bond energies, that is, of the difference in steric hindrances on a hydrogen atom in ethane and methane. Strictly speaking, however, this is incorrect as the removal of a hydrogen atom from the two molecules has probably altered to a different extent the bonding energies of the remaining atoms. Nevertheless only the first procedure can be followed through consistently with the available data and it will be used therefore in the following.

From Rossini's¹⁷ combustion data the following thermochemical equations can be set up

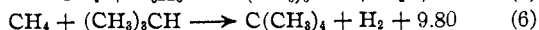
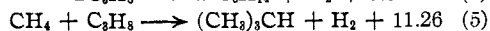
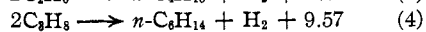
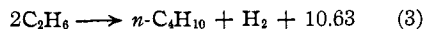


(15) The as yet unpublished measurements on the gaseous heat capacities of these compounds indicate that at absolute zero their energy difference is even larger.

(16) Parks, Huffman and Thomas, *THIS JOURNAL*, **52**, 1032, 4381 (1930).

(17) Rossini, *Bur. Standards J. Research*, **6**, 37 (1931); **12**, 735 (1934); **13**, 201 (1934); *J. Chem. Phys.*, **6**, 168 (1938). Room temperature data referring to the gaseous state have been used here and in the following. A conversion to absolute zero is so uncertain for most of the compounds considered that the accruing theoretical improvement would be wholly fictitious. We do not believe that such a conversion will change the results significantly.

(14) Kharasch, *Bur. Standards J. Research*, **2**, 359 (1929); Rossini, see references below.



The reactions involved all consist in the severance of two C-H bonds and a formation of an H-H and a C-C bond, the changes in the heats therefore being due exclusively to the variable steric hindrance. To what extent this latter may rise under exceptional circumstances is brought out by the calorimetric measurement of Bent and Cuthbertson:¹⁸ $2(C_6H_5)_3CH \rightarrow (C_6H_5)_3C-C(C_6H_5)_3 + H_2 + 40$ kcal.

The heats of reactions (3) and (4) are sufficiently near together to justify an assumption that only substitutions on the same atoms to which the bonds considered belong have substantial effects on the *relative* magnitude of steric hindrance. This assumption is in accord with conclusions drawn by Rossini.¹⁷

Using the following notation

A : energy of severance of a C-H bond in methane

A-X: energy of severance of a C-H bond in ethane (or primary C-H bonds in higher homologs)

A-Y: energy of severance of a secondary C-H bond in propane

A-Z: energy of severance of a tertiary C-H bond in isobutane

B : energy of severance of a C-C bond in ethane

B-x: energy of severance of a C-C bond in propane

B-y: energy of severance of an internal C-C bond in butane

B-y': energy of severance of a C-C bond in isobutane

B-z: energy of severance of a C-C bond in neopentane

one obtains from equations (1) to (6)

$$\text{from (1) - (2) : } X - x = 2.26 \text{ kcal.} \quad (7)$$

$$\text{from (1) - (3) : } 2X - y = 4.91 \quad (8)$$

$$\text{from (1) - (5) : } Y - y' = 4.28 \quad (9)$$

$$\text{from (1) - (6) : } Z - z = 5.74 \quad (10)$$

The simplest assumption concerning steric hindrance is to treat the effects of substituent alkyl groups as additive, so that $Y = 2X$; $Z = 3X$; $y = 2x$; $y' = 2x$; $z = 3x$. The following are the results

$$\text{from (1) - (2) : } X - x = 2.26 \quad (11)$$

$$\text{from (1) - (3) : } X - x = 2.45 \quad (12)$$

$$\text{from (1) - (5) : } X - x = 2.14 \quad (13)$$

$$\text{from (1) - (6) : } X - x = 1.91 \quad (14)$$

The assumption of additivity of the steric effects evidently is fairly but not completely successful. Better agreement can be obtained, of course, by using more parameters but their introduction would be difficult to justify.

(18) Bent and Cuthbertson, *THIS JOURNAL*, **58**, 170 (1936).

As seen above, thermal data on saturated hydrocarbons alone cannot disentangle the steric effects upon the C-H and the C-C bonds, only a difference appearing in the final equations. This is true of all thermochemical data, barring direct measurements of the heats of formation of free radicals; therefore an assumption is required to obtain individual values. One which we shall make is that the entire observed effect of alkyl substituents upon the heats of addition reactions to unsaturated hydrocarbons is due to their steric hindrance on the newly formed bonds (*cf.* p. 9). This means that their effect upon a $=CR_1R_2$ group is equal to their effect upon the group $-CHR_1R_2$ resulting from hydrogenation.

From the heats of hydrogenation of various olefins the mean effect of substitution of one alkyl group into ethylene is found equal to 2.6 kcal. (± 0.1). Substitution of the second alkyl group in symmetric position lowers the heat of hydrogenation by another 2.3 kcal. (± 0.1) if the heat of hydrogenation of the equilibrium mixture of the isomeric pentenes-2 or butenes-2 is taken for this calculation. This choice is justified by the consideration that the resultant normal pentane or *n*-butane has presumably approximately the same proportions of the *cis*- and the *trans*-configurations as the olefins.

The introduction of the third methyl group lowers the heat evolution by 1.0 kcal. and the fourth decreases it another 0.3 kcal. The trend of these figures is qualitatively the same as that observed in equations (11) to (14) but the quantitative agreement is imperfect, showing the crudeness of the underlying assumptions. Taking for the differential effect of a methyl group upon a C-H bond (*X*) the mean of 2.6 and 2.3 kcal., 2.45 kcal., and substituting into equation (11) or (12) one finds that *x* is very nearly zero, hence that the energy of the C-C bonds is constant in saturated hydrocarbons. The energy of the multiple carbon-carbon bonds is similarly independent of substitution since an identical differential effect of methyl groups has been assumed for all carbon-carbon bonds and has now been found equal to zero.

Heats of bromination (VII) reveal with the aid of the same assumption as above that for the C-Br bond the order of the hydrogen and the methyl group hindrances is reversed, the former hindering more, the quantity corresponding to *X* in equation (11) being *ca.* - 0.5 kcal. In the same

manner Rossini's combustion data on primary alcohols¹⁹ show that the methyl groups have lesser steric hindrance on the C-O bond. It seems that the relative steric effectiveness of hydrogen atoms and of methyl groups is correlated with the polarity of the bond on which the hindrance is exercised.

Some years ago Eyring²⁰ made an approximate wave-mechanical calculation of the interactions between non-bonded atoms in methane and in ethane, concluding that in the latter, because of greater steric hindrance of a CH₃ group, the C-H bond is effectively weaker by 3 kcal. On the preceding pages 2.5 kcal. was estimated for the same effect in excellent agreement with Eyring's calculation. To reduce the mathematical complexity of the problem, Eyring had to make several drastic simplifications, in view of which and of the frequent failure of approximate quantum mechanical calculations to obtain accurate interaction energies at close distances of approach, the agreement of his and of the present values is surprising; we are inclined to regard it as somewhat accidental because in other details Eyring's calculation does not agree so well with experimental data.

4. Hindrance of Internal Rotation.—According to Eyring the energy difference between the staggered and the eclipsed configurations of ethane is only 0.35 kcal., while observations give 2.75 kcal.¹³ This large discrepancy has now led him to suggest²¹ that some other effects are responsible for the hindrance of internal rotation. However, the general steric hindrance and the hindrance of internal rotation change in such analogous manner from case to case that the introduction of new effects seems rather unnecessary. Methyl groups were shown above to exert greater steric hindrance upon C-H bonds and parallel to this it is found that the hindrance of internal rotation changes from 2.75 kcal. in ethane to approximately 3.2 kcal. in propane,^{22,23} 3.8 in isobutane²² and 4.2 in neopentane.²² In propylene^{22,23} the hindrance of internal rotation was found equal to only 0.8 kcal., indications being that only three angular positions of minimum potential energy exist for the methyl group. This suggests, in accord with the facts to be considered later, that the steric

effect of a =CH₂ group is not much larger than that of a hydrogen atom or a methyl group, although the existence of only three equilibrium positions, if confirmed, must be in addition explained by some special properties of a double bond (*cf.* ref. 23). The consideration of the case of cyclopentane has shown that the staggered position of C-H bonds is that of lower energy, which again agrees with steric hindrance as the cause of the hindrance of internal rotation.

Between the two alternatives: postulating different mechanisms for the steric hindrances and for the hindrances of internal rotation or considering Eyring's calculations as only qualitatively correct, we prefer the second. To reconcile various facts cited above with calculations of the type made by Eyring, the energy of repulsive interactions should be made a steeper function of distance and be made larger at short distances.

5. Energies of Steric Hindrance.—Some facts which we shall consider now suggest indeed that steric hindrance by atoms bonded to the same carbon upon another of its bonds is considerably larger than the 2.5 kcal. calculated by Eyring for a hydrogen-hydrogen interaction in methane.

The hydrogenation of the first double bond in allene evolves 11 kcal. more heat than the hydrogenation of propylene. To correlate this observation with other discussed facts we suppose again that the steric hindrance of a methylene group is not much larger than that of a methyl group or even of a hydrogen atom. Then the large heat evolution in the reaction of allene is obtained because the secondary hydrogen in the resultant propylene has no other hydrogen neighbors on the same carbon, while the primary hydrogen of the methyl group has steric hindrance from only one hydrogen atom on the adjacent carbon. It is, of course, impossible to separate all these effects, but an estimate of something of the order of 9 kcal. for the hydrogen-hydrogen interaction on the same carbon seems not unlikely, considering that this interaction occurs over the shortest distance.

The preservation of tetrahedral angles in halogenated methanes occasionally has been cited as evidence of rather weak interactions between non-bonded atoms, but actually this evidence merely shows that the difference between interactions of a halogen with another halogen and with hydrogen is rather small. This conclusion is confirmed by many other facts, only the obser-

(19) Rossini, *J. Research Natl. Bur. Standards*, **13**, 189 (1934).

(20) Eyring, *THIS JOURNAL*, **54**, 3191 (1932).

(21) Abstracts of papers presented at the Baltimore meeting of A. C. S., April, 1939.

(22) Pitzer, *J. Chem. Phys.*, **5**, 473 (1937).

(23) Kistiakowsky, Lacher and Ransom, *ibid.*, **6**, 900 (1938).

vations of Beach and Palmer²⁴ on the strong hindrance of internal rotation in *sym.* dihalogenethanes being possibly in disagreement with it.

The manner in which the absolute magnitude of the steric hindrances could be found would be by removing some of the atoms present. Fortunately this is at least approximately realized in molecules in which the carbon atom forms a double bond and indeed spectroscopic evidence²⁵ points strongly to the H-C-H angle being greater than the tetrahedral value in formaldehyde and in ethylene. It may be argued, of course, that this is the "natural" configuration of carbon bonds, when one of them is double, but until this is conclusively proved we choose to think that the increase of the angle is due to repulsions between hydrogen atoms.

Considerable interest has been aroused by the finding of Herzberg that in methylacetylene the single carbon-carbon bond is appreciably shortened in comparison with those in saturated compounds.²⁶ Similar observations have been since made on the C-Cl and C-Br bonds in halogenated acetylenes²⁷ and the effect has been ascribed to resonance. Pauling²⁸ has pointed out that resonance cannot account for a decrease of the C-H distance in acetylene as compared with that in methane and yet, as Table V shows, the fractional change of the bond distances is nearly the same in all observed cases. The slight increase of the effect from the C-H to the C-Br bond is quite likely due to additional contribution of resonance, manifested by the changed dipole moments of the carbon-halogen bonds in acety-

TABLE V
EFFECT OF ADJACENT CARBON-CARBON BONDS UPON
INTERATOMIC DISTANCES

	Single, Å.	Triple, Å.	S:T ratio
C-H	1.093 ^a	1.058 ^b	1.034 (± 0.005)
C-C	1.54 $\pm 0.03^c$	1.463 ^d	1.051 ($\pm .025$)
C-Cl	1.77 $\pm .02^e$	1.68 $\pm 0.04^e$	1.052 ($\pm .035$)
C-Br	1.91 $\pm .02^e$	1.80 $\pm .03^e$	1.060 ($\pm .028$)

^a Ginsburg and Barker, *J. Chem. Phys.*, **3**, 668 (1935).

^b Herzberg and Spinks, *Z. Physik*, **91**, 386 (1934). ^c Brockway, *Rev. Mod. Phys.*, **8**, 231 (1936). ^d Herzberg, Patat and Verleger, *J. Phys. Chem.*, **41**, 123 (1937). ^e Brockway and Coop, *Trans. Faraday Soc.*, **34**, 1429 (1938).

(24) Beach and Palmer, *J. Chem. Phys.*, **6**, 639 (1938).

(25) Dieke and Kistiakowsky, *Phys. Rev.*, **45**, 4 (1934); Badger, *ibid.*, **45**, 648 (1934); Penney, *Proc. Roy. Soc. (London)*, **A144**, 166 (1934).

(26) Herzberg and Spinks, *Z. Physik*, **91**, 386 (1936); Herzberg, Patat and Verleger, *J. Phys. Chem.*, **41**, 123 (1937).

(27) Brockway and Coop, *Trans. Faraday Soc.*, **34**, 1429 (1938).

(28) Pauling, Springall and Palmer, *THIS JOURNAL*, **61**, 927 (1939).

lenes. For the C-H bond, however, wholly and for the C-C bond predominantly, we consider the reduced steric hindrance by adjacent atoms to be the cause of bond shortening in acetylenic compounds.

This requires that a $\equiv\text{CH}$ group exercise much smaller steric hindrance than do three hydrogen atoms in methane, a conclusion which is a natural extension of the earlier remarks on the effect of a methylene group. If the steric effects of a $-\text{CH}_3$, $\equiv\text{CH}_2$ and a $\equiv\text{CH}$ group upon a C-H or a C-C bond do not differ greatly, then one may perhaps conclude also that the difference in the steric effects of a hydrogen atom and a methyl group upon all these groups is approximately the same. Such a conclusion is supported by data of Table IV and already has been made use of in section 3.

A numerical relation between bond length and bond energy, similar to those between bond length and the force constant, is not known, but one can surmise that a reduction of the bond length by some 3 to 4% causes much more than a proportionate increase in the bond energy. Hence repulsive interactions between atoms in methane must reduce the energy of the "isolated" C-H bond by a considerable amount.

In ethylenic compounds the C-H and the C-C bond length should be the mean of those in acetylene and in ethane, that is, 1.075 and 1.50 to 1.51 Å., respectively. The former would require the H-C-H angle in formaldehyde and in ethylene to be about 120°. It is claimed that in ethylenic compounds the C-C distance is the same as in paraffins but a difference of 0.04 Å. is so close to the admitted experimental error (0.03) that the evidence of electron diffraction is not yet conclusive.

In the partial hydrogenation of butadiene and other dienes, the added secondary hydrogen atom is subjected to steric hindrance by the group $-\text{CH}=\text{CH}_2$ rather than by $-\text{CH}_2-\text{CH}_3$ as in the hydrogenation of olefins. According to what has been said before, this means lower steric hindrance and hence higher heat of hydrogenation. Therefore resonance energies calculated in the beginning of this discussion by a simple procedure should be increased by 1 or even as much as 2 kcal. (*cf.* discussion of allene) which would bring their absolute magnitude into better agreement with theoretical values calculated by Lennard-Jones¹² and Coulson.²⁹

(29) Coulson, *Proc. Roy. Soc. (London)*, **A164**, 383 (1938).

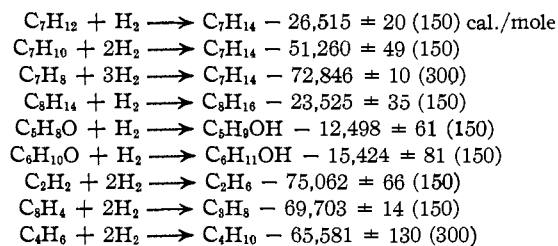
We have restricted our discussion to the simplest organic compounds because only for them reliable thermochemical and structural data exist, but one could readily extend it *ad infinitum* by borrowing from the more qualitative organic evidence. Concluding, we wish to stress that steric hindrance in the sense discussed above is generally responsible for the effects of substituents upon the "standard" properties of functional groups in polyatomic molecules and that therefore it is rightly placed next to resonance in importance as the source of variety among organic compounds.

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Summary

The following heats of hydrogenation have been determined. All data refer to 355°K. in the gaseous phase.



A consideration of the entire work on the heats of addition reactions and of other experimental data found in the literature reveals the large magnitude of steric hindrances exercised by non-bonded atoms in simple organic molecules. These repulsive interactions are stronger than supposed hitherto and contribute largely to the variation in the properties of the functional groups.

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Internal Rotation and Resonance in Hydrocarbons

BY EVERETT GORIN, JOHN WALTER AND HENRY EYRING

Introduction

Recent experimental evidence indicates the existence of a potential barrier of the order of 3000 cal. restricting the rotation of the methyl groups about the C-C bond in ethane. The data on the specific heat of ethane gas at low temperatures¹ and the entropy of ethane as determined both from the third law and from the hydrogenation of ethylene are in accord with this assumption.² The structure of the rotation bands in the ethane spectrum has also been interpreted as indicating a barrier of at least 2000 cal.³

On the other hand the repulsion due to the hydrogen atoms calculated according to standard

(1) Kistiakowsky and Nazmi, *J. Chem. Phys.*, **6**, 18 (1938); Hunsman, *Z. physik. Chem.*, **B39**, 23 (1938); Wilson, *J. Chem. Phys.*, **6**, 740 (1938); see, however, Eucken and Weigert, *Z. physik. Chem.*, **B23**, 265 (1933).

(2) Smith and Vaughan, *J. Chem. Phys.*, **3**, 341 (1935); Teller and Topley, *J. Chem. Soc.*, 876 (1935); Kemp and Pitzer, *THIS JOURNAL*, **59**, 276 (1937).

(3) Howard, *J. Chem. Phys.*, **5**, 451 (1937).

quantum mechanical procedure for the usual valence bond structure yields a potential barrier of 300 cal. with a minimum corresponding to the staggered position of symmetry D_{3d} . In this calculation the van der Waals attractive potential between hydrogens was taken as $101/R^6$.⁴

It was pointed out by Penney⁵ that with the Slater-Pauling model for the carbon bond in ethane the repulsions taken account of in the above calculation are the only ones present if we use the single valence structure.

Barrier Height if Protons Replace Hydrogen Atoms.—If we suppose the hydrogen atoms be replaced by protons, the structure otherwise remaining unchanged, the potential barrier from the coulomb repulsions is 5200 cal. with a minimum in the staggered position. This is of course an upper limit and a more exact calculation than

(4) H. Eyring, *THIS JOURNAL*, **54**, 319 (1932).

(5) W. G. Penney, *Proc. Roy. Soc. (London)*, **A144**, 166 (1934).