unsuccessful. Reduction with hydrazine according to Staudinger[11] was tried without success.

Clemmensen Reduction of the Ketone Acetate: Desoxy Diphenyl Carbinol V.—The above ketone acetate (390 mg.) was refluxed for seven hours with 1.2 g. of amalgamated zinc in 25 cc. of alcohol and 7 cc. of 8 *N* hydrochloric acid. The solid material obtained on diluting the filtered solution with water yielded no crystals and was refluxed for one-half hour with alcoholic alkali for saponification. The solid which precipitated on dilution was dried and crystallized from ether–hexane, the solution depositing glistening prisms mixed with slightly gummy, fine, felt-like needles. The prisms were separated mechanically (m. p. 224–226°) and recrystallized repeatedly from ether–hexane, giving 20 mg. of satisfactory material, m. p. 226–228° (well dried). The composition is approximately that of the desired **desoxy diphenyl carbinol**.

Anal. Calcd. for $C_{34}H_{46}O_2$: C, 83.90; H, 9.53. Found: C, 84.26; H, 9.04.

The slightly gummy needles (180 mg.) could not be freed completely from the above material by repeated crystallization from ether–hexane. Acetylation gave a resin and this on saponification gave an intractable mixture separating from methanol in clusters of small needles and soft wax-like nodules.

Summary

Conditions have been found for the reduction of sarsasapogenone to desoxysarsasapogenin in good yield by the Clemmensen method without alteration of the side chain. A preliminary account is given of a new C_{27}-acid obtained by the oxidation of desoxysarsasapogenin with chromic acid, and further observations are reported on the degradation of the hydroxy lactone $C_{22}H_{34}O_3$.

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CAMBRIDGE, MASS.
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[11] Staudinger, *Ber.*, **44**, 2204 (1911).

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF HARVARD UNIVERSITY]

Heats of Organic Reactions. VII. Addition of Halogens to Olefins

BY JOHN B. CONN, G. B. KISTIAKOWSKY AND ELGENE A. SMITH

It has been shown in the earlier papers of this series[1] that the heats of addition of hydrogen to the olefinic bond vary in a regular manner with the constitutional make-up of the rest of the molecule. It seemed highly desirable to investigate whether these variations are specific for hydrogenations or are characteristic generally of addition reactions opening the ethylenic bond. The reaction with halogens was selected to test the question because of its convenience and the lack of accurate combustion data on dihalides. Another reaction considered, the addition of hydrogen halides, had to be discarded because we were unsuccessful in creating catalytic conditions under which this reaction occurs rapidly in the gas phase at temperatures below *ca.* 150°, the upper limit of usefulness of the present calorimeter. The results to be presented here unfortunately are neither as reliable nor as extensive as those on the heats of hydrogenation; nevertheless, even allowing for all possible errors, they are many times more accurate than the available combustion data.

Method and Compounds

The calorimeter itself and the general procedure were the same as described in the first paper of this series and only changes need to be recorded.

To avoid premature reaction, bromine or chlorine was carried to the calorimeter through a separate conduit in a stream of inert gas and mixed with excess hydrocarbon in the catalyst chamber within the calorimeter. Upon reaction and heat exchange the gases passed through a valve which directed the stream either to a cold trap for collection of a sample and tests for completeness and cleanliness of the reaction (in the fore- and after-periods), or, during the calorimetric run, to a jet where the gases were burned in excess oxygen and the halogens determined as such and as hydrogen halides.

The halogens were contained in an efficient spiral bubbler, kept at constant temperature (ice for bromine, Dry-Ice and alcohol for chlorine), through which passed a metered stream of inert gas (carbon dioxide with bromine, argon with chlorine).[2] Frequently additional inert gas was by-passed around the bubbler and added to the main gas stream to dilute the reaction mixture and so avoid the condensation of the product in the calorimeter. The hydrocarbon vapor also was metered, so that a condition of constant gas flow prevailed in the calorimeter during a run.

Several substances have been tried for their catalytic effect on the halogenation reaction, the choice being finally calcium bromide and calcium chloride for the bromination and the chlorination, respectively. Glass wool, asbestos, platinized asbestos, ferric halides, bismuth halides and activated charcoal were also experimented with but discarded either because of insufficient activity at the temperatures in question (around 100°) or because substitution reactions took place with the hydrocarbons used. The catalysts were made by evaporating a solution of cal-

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[1] THIS JOURNAL, **57**, 65 (1935); **57**, 876 (1935); **58**, 137 (1936); **58**, 146 (1936); **59**, 831 (1937); **60**, 440 (1938).

[2] Nitrogen had to be avoided since nitrogen oxides are formed in the free flame used in the analytical system, and disturb the analysis.

cium halides (30%) with cleaned asbestos fibers (70%) and drying above 100°.

The conditions in the calorimeter were maintained such that a complete reaction of the halogen occurred, the exit gases being a mixture of the inert gas, the excess hydrocarbon and the dihalide. Because of this, a determination of the total halogen content of the gases sufficed to find the amount reacted. Figure 1 shows semi-schematically the analytical setup. After leaving the control valve the reacted gases entered a quartz jet and burned there in an excess of oxygen; some hydrogen was added to the combustible gases to ensure a healthier flame. The ignition was started by a spark-coil, the current being turned on a few seconds before turning the valve. Immediately surmounting the flame vessel was a quartz tube in a furnace maintained at bright red heat; this tube was filled with chips of porcelain, which ensured the combustion of the organic material and completed the conversion of the halogens to the free state or to the form of hydrogen halides. From the furnace the gases passed a trap in a Dry-Ice or ice-bath, surmounting which was a tower filled with glass beads and solid potassium iodide. Finally there was a bubbler filled with a potassium iodide solution which acted, however, merely as an indicator that absorption of halogens was complete. After the run the furnace was flushed with nitrogen and the connecting tubing flamed to distil the condensed water into the trap. The contents of the tower were then washed into the trap with potassium iodide solution and water, and the whole was made up to a liter. Aliquot parts were titrated with thiosulfate solution; the sample was then brought to boiling, cooled and potassium iodate added; a second titration with thiosulfate followed. In case of bromine the fraction present as hydrogen bromide was usually quite small (about 5%), but with chlorine the acid constituted the bulk of the product (*ca.* 95%).

Ordinarily two titrations were made on each run, but in the few cases when they disagreed by more than 0.1%, repeated titrations ensured the reliability of the result to better than that figure.

The thiosulfate solution was standardized with potassium bromate according to accepted procedure,[3] the results of repeated determinations agreeing to within 0.05%.

Before the calorimetric work was started, various tests of the analytical setup with weighed samples of pure organic halides showed that results correct to nearly 0.1% could be expected. Thereupon other preliminary work and calorimetric runs were undertaken, which occupied the fall and winter of 1937–1938. When the series of brominations was completed, the tests with weighed samples were done again, but to our considerable dismay it was discovered that losses of halogen to the extent of 0.5 to 1.0% occurred somewhere. Extensive search for sources of this error traced it finally to a coating of platinum on the porcelain chips in the furnace, which was present there from the work on hydrogenations. It is very difficult to explain why the same furnace gave satisfactory results a year earlier, the only possibility being that its temperature may have changed in the meantime. The mechanism by which the halogens are removed from the gas stream is also puzzling since the small amount of a solid distillate from the furnace was always flamed after the run to ensure its decomposition, the remainder appearing to be metallic platinum.

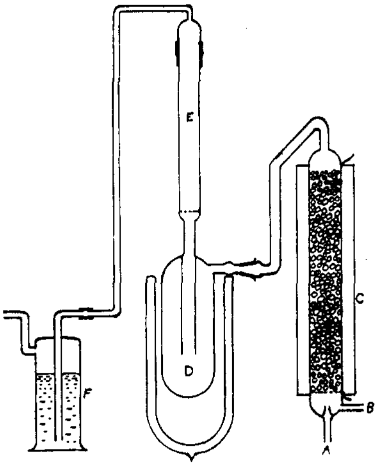

Fig. 1.—A, gas inlet; B, oxygen inlet; C, porcelain filled quartz furnace; D, cold trap; E, moist potassium iodide-glass pearl filled absorption tower; F, bubbler of 10% potassium iodide solution.

Nonetheless, whatever the precise cause of the failure of the original furnace, its repacking with clean porcelain remedied the situation, as shown in Table I, which presents the data on runs with weighed samples of organic halides and of molecular bromine. These samples were contained in sealed thin-walled glass ampoules placed in the gas stream instead of the calorimeter, and were broken after the flame was started, the rest of the procedure and the composition of the gases (except for the halogen, of course) being essentially the same as in ordinary calorimetric runs. Table I contains all runs made with sealed samples, none being discarded for "inconsistency" of the result. The runs with molecular bromine give the best agreement, then follow runs with ethylene dibromide which are also good; small losses of chlorine are noted in runs with ethylene dichloride but these, we believe, are within experimental uncertainties of the method. How-

TABLE I

Sample	Sample, g.	Moles of halogen recovered, × 10^3	Error of analysis, %
Br_2	0.9794	6.137	−0.07
Br_2[a]	1.5556	9.753	+0.20
$C_2H_4Br_2$	1.6994	9.034	−0.15
	1.4568	7.760	+0.06
$C_4H_8Br_2$	1.0496	4.836	−0.51
	1.4040	6.472	−0.47
	1.6234	7.481	−0.51
$C_2H_4Cl_2$	0.7826	7.873	−0.43
	0.6857	6.918	−0.26
	1.3767	13.883	−0.21

Ethylene present in the gas stream.

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[3] Treadwell and Hall, "Quantitative Analyses," John Wiley and Sons, Inc., New York, N. Y., 1928, Vol. II, p. 554.

TABLE II

HEATS OF HALOGENATION REACTIONS

Hydrocarbon	Expts. made	Preliminary $-\Delta H_{355°}$	n^{20}_D product measured	Literature	Final $-\Delta H_{355°}$ $\frac{\text{cal}}{\text{mole}}$
			A. Bromination		
C_2H_4	13	29,231 ± 100	1.5380 ± 0.0001	1.5379	29,058 ± 300
C_3H_6	5	29,585 ± 29	1.5199 ± .0001	1.5203	29,412 ± 200
C_4H_8-1	3	29,758 ± 3	1.5150 ± .0001	1.5150[4]	29,585 ± 200
trans-C_4H_8-2	1	29,148	1.5113	1.5116[4]	29,075 ± 200
cis-C_4H_8-2	3	30,350 ± 23	1.5149 ± .0001	1.5147[4]	30,177 ± 200
Trimethylethylene	2	30,577 ± 2	1.5054 ± .0003		30,398 ± 200
			B. Chlorination		
C_2H_4	3	43,653 ± 27	1.4443 ± .0003	1.44432	43,653 ± 150

ever, the very constant shortage of bromine in dibromobutane is outside the analytical errors and must be due to a slight impurity of the compound used for analysis (redistilled dibromide prepared for this work). This is best demonstrated by a run in which molecular bromine in the sealed ampoule and ethylene in the gas stream were used. Before the gases reached the analytical unit, the conversion of bromine to ethylene bromide was nearly complete and yet no shortage of bromine developed.

At the time of the discovery of the analytical errors, the still available quantities of pure hydrocarbons were so limited that a repetition of the entire series of brominations would have required new preparations of several of the olefins. To avoid this we have chosen to sacrifice somewhat the final accuracy of the data, making only one run on each of the olefins with the corrected combustion furnace. The average difference between the new runs and the old averages was used to correct the latter. This presumes that the furnace was misbehaving in the same manner during the entire series of brominations and thus introduces a not excessively large but nevertheless a considerable additional uncertainty.

Chlorination runs were made after the refilling of the furnace and therefore no analytical uncertainty impairs these results.

Bromine used for the reaction was Mallinckrodt analytical grade; iodimetric titration gave the correct molecular weight but no further tests or purification were undertaken.

Chlorine was distilled into the spiral bubbler directly from a used tank.

Excepting ethylene and propylene the hydrocarbons used were samples remaining from the work on hydrogenations; their description is superfluous.

Ethylene and propylene were generously presented to us by the Linde Air Products Company and were subjected by them to fractional distillations; the former is rated as 99.88% pure, the latter as 99.89% pure.

It is to be noted that in contrast to our work on hydrogenations, the method of analysis here devised is such that small amounts of saturated hydrocarbons in the material used have no effect on the results. Even the presence of minor olefinic impurities is of very small import because the heats of bromination, as will be seen presently, change only slightly with the nature of the olefin.

Results

The two important chemical sources of error in the measurement of brominations and chlorinations by the method here outlined are the incompleteness of the reaction and the occurrence of substitution. Fortunately, both are readily detected, one by introducing into the stream of exit gases a Congo Red paper, the other by introducing a paper moistened with starch–potassium iodide solution. Both these tests were applied before and after each run and were so sensitive that 0.1% of the original halogen present as such or as hydrogen halide, could have been detected readily. Only runs in which both tests were negative are reported in the following. Samples of the dihalides were collected and their refractive indices taken, but no freezing curves studied.

Table II presents a summary of the results obtained in the brominations and chlorinations. The literature values for the refractive indices are from "I. C. T." except where otherwise stated. Where more than one experiment was performed on a compound, both the rate of flow of the gases through the calorimeter and the bromine:olefin ratio were varied, but no systematic trends in the heats were observed. The deviations from the given heats of halogenation in the column of "preliminary values" represent the average deviations from the mean values; the deviations from the final values are estimated total probable errors. Deviations of the measured refractive indices from the given figures are maximum deviations of individual samples from the mean.

The experiments with ethylene extended during a period of over four months, many adjustments and minor changes of technique being made between successive runs. Undoubtedly the earlier mentioned losses of bromine did not remain quite constant, which accounts for the rather large

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(4) Dillon, Young and Lucas, THIS JOURNAL, 52, 1953 (1930).

deviations from the mean. It is preferable, however, to use all these runs in forming the average since no safe clue is available for a rejection of some runs.

In experiments with propylene and higher hydrocarbons a Dry-Ice trap was placed in the gas stream before it reached the Congo Red paper, since otherwise a hydrolysis of the bromide caused a change in color of the test paper. In experiments with trimethylethylene difficulty was experienced in freeing the sample of the dibromide from the unreacted olefin and the product turned purple on standing in the air, presumably due to a loss of hydrogen bromide and rearrangement to a ketone caused by the moisture of the air.

Cyclohexene and isobutene could not be brominated because in both cases substitution took place. With the latter hydrocarbon much methallyl bromide was recovered.

Propylene and higher hydrocarbons could not be chlorinated successfully because substitution took place to an extensive and variable degree. No catalyst could be found to promote the quantitative chlorination of *cis*- and *trans*-dichloroethylenes at the temperature of the calorimeter.

Table III presents the results obtained in the bromination reaction with the repacked furnace and shows the deviations of the new results from the averages of the "preliminary" column of Table II. The deviations are not very constant, but an estimation on the basis of all available data suggests that they are not outside the limits of possible accidental errors. This is demonstrated best by a comparison of the propylene and the butene-1 reactions, the products of which surely will undergo combustion in much the same manner. These two series of runs followed one another and thus the furnace should have behaved also quite similarly. And yet the variations between the earlier and the new experiments with the two compounds differ appreciably. It is therefore preferable to interpret all variations in the fourth column of Table III as accidental and take their average for the correction of the third column of Table II. The so calculated values are given in the last column of Table II.

TABLE III

BROMINATION WITH THE CORRECTED ANALYTICAL PROCEDURE

Hydrocarbon	Expts. made	$-\Delta H_{355°}$ cal./mole	Diff. from the mean of Table II cal./mole
C_2H_4	1	29,126	−105
C_3H_6	1	29,277	−308
C_4H_8-1	1	29,682	− 76
trans-C_4H_8-2	1	28,945	−203
			Mean −173

It may be noted that no more trimethylethylene and *cis*-butene-2 were available at the time of the repeat runs and therefore the average from the other hydrocarbons in Table III was used to correct the data of Table II.

Discussion of the Results

Since the heat of addition of chlorine to ethylene was measured after the alteration of the analytical furnace, no significant systematic error should be involved in the results and the error of the average is of the same order of magnitude as the mean deviation and not more than 0.3%.

The same is not true for brominations: first, the individual values show greater scattering, due no doubt to the somewhat irreproducible losses of bromine in the platinum coated furnace; second, a semi-systematic error is introduced in correcting for bromine losses. The uncertainty from the first cause can be estimated as 0.3% (except for ethylene, where a slightly larger value is used), that from the second, as not more than 0.7%; altogether, then, somewhat less than 1%.

These imperfections, fortunately, do not disfigure the results to an extent large enough to void any of the following deductions; they leave the new data decidedly superior in accuracy to values which can be derived from combustion heats. A perusal of the standard reference works reveals that extremely little has been done on combustion of dihalides derivable from olefins by addition of halogens. In fact, the only available data are on ethylene dihalides, which have been summarized by Bichowsky and Rossini.[5] Using their values, the heats of the gaseous additions are found readily

$$C_2H_4 + Cl_2 = C_2H_4Cl_2 - 40.3 \text{ kcal.}$$
$$C_2H_4 + Br_2 = C_2H_4Cr_2 - 29.2 \text{ kcal.}$$

The agreement of these values with those here reported is as good as could be expected.

The series of olefins investigated in the bromine reaction is not very extensive but it includes those essential compounds, the study of which previously led to the establishment of the regularities of the heats of hydrogenation. It is possible, therefore, to draw a rather interesting conclusion that

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(5) Bichowsky and Rossini, "Thermochemistry of Chemical Substances," Reinhold Publishing Corp., New York, N. Y., 1936.

the trend of the heats of the two reactions is in the opposite direction when the substitution on the ethylenic group is changed; with increasing substitution the heats of hydrogenation show a very decided decrease, the heats of bromination, on the other hand, show a less pronounced increase. This is brought out very clearly in Fig. 2.

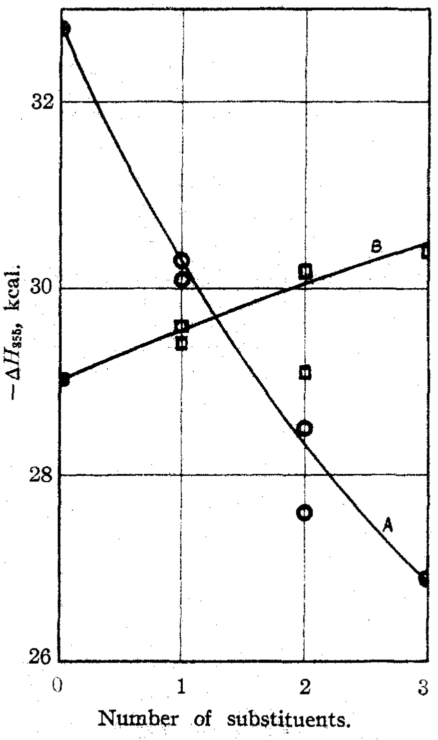

Fig. 2.—The effect of substituents on the heats of reactions: curve A, hydrogenations; curve B, brominations.

Some time ago it was suggested that the heats of iodination of olefins follow the same trend[6] as the heats of hydrogenation. This conclusion was reached, however, on the basis of rather limited and not too accurate experimental material and must be revised in view of the present findings on the heats of brominations. The iodination of butene-1 is in reality probably more exothermic than that of ethylene. This conclusion can be reconciled with the experimental data presented in the cited work; consequently the entropy changes in the two reactions are significantly different.

The opposite trends in the hydrogenation and halogenation reactions suggest that the changes themselves are due not so much to variations in the strength of the ethylenic bond as to variable bond strengths of the addenda; they must be subject to constitutional influences from the groups attached to the ethylenic system. These effects may be termed for short steric, although a naïve interpretation based on the volume requirements of the different atoms and radicals involved leads to completely wrong conclusions. Indeed, a replacement of the small hydrogen atoms by the more bulky methyl radicals in ethylene, reduces the heat of addition of the small hydrogen atoms but enhances that of the larger bromines. A qualitatively correct interpretation is offered by considerations of electrostatic induction effects. The replacement of an electropositive hydrogen atom by a more electronegative methyl radical should make the ethylenic carbon atom more electropositive and therefore favor the addition of bromine, making the addition of hydrogen less exothermic. It is very doubtful, however, whether such effects are strong enough to account for some 6 kcal./mole change in the reaction heats and, besides, another effect must be included, the direct electrostatic attraction or repulsion of the atomic groups in ethylene on the addenda. Evidently this action will cause opposite trends in the reaction heats from those just deduced and the over-all effect is in doubt.

Whatever may be the correct atomistic interpretation of the results here described, they serve admirably to explain on a thermodynamic basis the so-called Markownikoff rule, which states that normally the addition of hydrogen halides to olefins occurs so that the halogen adds to a more highly substituted carbon atom. To give this interpretation a quantitative character, it is necessary to formulate a rule which may be stated as follows. The heat of addition to the ethylenic linkage is the sum of two nearly independent terms, the heats of addition to each of the two ethylenic carbon atoms. The heats of hydrogenation provide a sound basis for this rule; they show that, except for effects of conjugation, only atoms or radicals once removed in the molecule have significant effects upon one another. Upon addition to the ethylenic bond, however, the addenda are twice removed from each other and therefore only minor interaction should be expected between them.

The lowering of the heat of hydrogenation in going from ethylene to propylene means therefore that less heat is evolved on adding hydrogen in a secondary position, the lowering being equal to the

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(6) Cline and Kistiakowsky, *J. Chem. Phys.*, **5**, 990 (1937).

difference in observed reaction heats. On the contrary, an increase of the heat of bromination means that the addition of bromine in a secondary position is accompanied by more heat evolution than that in the primary one.

Reasoning in this manner it is possible to account for all our previous observations to about 1 kcal. accuracy, which is therefore to be considered as the accuracy of the enunciated rule.

If the rule is generally correct, then the heat of addition of hydrogen halide must be an average of the heats of addition of hydrogen and halogen, corrected by the heat of formation of the hydrogen halide. Using combustion data this comparison may be made and is shown in Table IV. The values of the first column of heat data were all derived from figures given by Bichowsky and Rossini;[5] the figures in the last column are averages of the observed heats of hydrogenation and halogenation, the heat of iodination being derived from equilibrium measurements[7] and therefore subject to a larger uncertainty. These data were converted to 25° by deducting 0.2 kcal. and corrected by the heat of formation of the hydrogen halide. The agreement of the two columns is well within the combined experimental errors, which shows that even a profound change of one of the addenda leaves unaltered the heat of addition of the other one.

TABLE IV

HEATS OF ADDITION OF HALOGEN ACIDS TO ETHYLENE

	From heats of combustion: ΔH, kcal./mole	Calculated ΔH in kcal./mole
$C_2H_4 + HCl = C_2H_5Cl$	−14.6	−15.9
$C_2H_4 + HBr = C_2H_5Br$	−17.9	−18.3
$C_2H_4 + HI = C_2H_5I$	−17.9 (?)	−21.4 (±1)

A further interesting case, which tests the rule, is the addition of hydrogen bromide to isobutene to form the tertiary bromide. The heat of this reaction has been calculated from the equilibrium measurements[8] and the value, 18.9 kcal./mole, is fairly accurate (±0.9 kcal.). The heat of addition of bromine to isobutene has not been measured but by analogy with hydrogenations it may be taken to be identical with the heat of bromination of *cis*-butene-2, *i. e.*, 30.0 kcal. at room temperature. The difference of this value from that found for ethylene (28.9) will be attributed to the addition on the tertiary carbon atom. Hence for this reaction we can write: isobutene + $^1/_2$ Br_2 (in tertiary position) = 30.0 − $^1/_2$(28.9) = 15.5 kcal. Hydrogen addition occurs in the primary position and therefore one half of the heat of hydrogenation of ethylene (16.3 kcal.) applies to this reaction. Together 31.8, and when this figure is corrected for the heat of formation of hydrogen bromide (Bichowsky and Rossini;[7] −12.4 kcal. from the gaseous elements), the result is 19.4 kcal. in excellent agreement with the directly measured figure.

The heats of addition of hydrogen chloride and hydrogen iodide to isobutene are 17.1[8] and 19.1[9] kcal., respectively. It is thus evident by comparison with Table IV that addition of chlorine or iodine in tertiary position is accompanied by an increased heat evolution similar to that discussed above for bromine.

Under normal conditions in the liquid reaction and certainly in the gas phase, the tertiary bromide is formed in preference to isobutyl bromide; this is according to the Markownikoff rule and, as we can now show, means that in the reaction the thermodynamically more stable compound results. Indeed, the heat of formation of isobutyl bromide, according to the enunciated rule, is made up of 14.4 kcal. for the addition of bromine in the primary position (as in ethylene) and 28.2 − $^1/_2$(32.6) = 11.9 for hydrogen (heat of hydrogenation of isobutene less one half the heat of hydrogenation of ethylene). Together 26.3 kcal., which, when corrected by the heat of formation of hydrogen bromide, gives 13.9 kcal. and shows that isobutyl bromide is considerably less stable than the tertiary compound, since its entropy cannot be so much larger as to overcome the exothermicity of the reaction to form the tertiary compound. In the cited work it was found that the equilibrium constant in the reaction isobutyl chloride–tertiary butyl chloride was somewhat larger than 10 at 270°. Assuming zero entropy change in the reaction between the bromides at 270°, an equilibrium constant of 10^2 is calculated in close agreement with the above value for the chlorides.[10]

On the whole it appears then that the Markownikoff rule, although it deals with the essentially kinetic problem of the relative rates of two competing reactions, can be correlated with the thermodynamic stability of the preferentially formed

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(7) Cuthbertson and Kistiakowsky, *J. Chem. Phys.*, **3**, 631 (1935).

(8) Kistiakowsky and Stauffer, THIS JOURNAL, **59**, 165 (1937).

(9) Jones and Ogg, *ibid.*, **59**, 1943 (1937).

(10) Similar conclusions can be drawn from the work of Brouwer and Wibaut [*Rec. trav. chim.*, **53**, 1001 (1934)] on the formation of and equilibrium between the primary and secondary propyl bromides and chlorides. See also Schjånberg, *Z. physik. Chem.*, **A172**, 197 (1935).

compound. It is obviously incorrect to postulate a close proportionality between the free energy decrease in a reaction and the rate at which it occurs, since too many exceptions to such a correlation can be cited. Nevertheless, in a series of homologous reactions a correlation of this type must frequently exist. Some cases have been discussed earlier.[11] Also in the field of catalytic reactions two instances may be cited; in the series of hydrogenations from ethylene to tetramethylethylene, studied calorimetrically, the heats of the addition decrease markedly; simultaneously the speed of the reaction on a given catalyst decreases also; thus the copper catalyst used could hydrogenate ethylene instantaneously even at 0°, but with tetramethylethylene it was ineffective even at 80° and the intermediate compounds fell in between these limits. On the other hand, the heats of bromination rise with increasing substitution; in parallel to this an increasing activity of the calcium bromide catalyst was observed.

Kharasch and others have cited instances when the Markownikoff rule breaks down, the condition apparently being that the reaction be catalyzed by oxygen or a peroxide. This effect is not noted in the gas phase reaction[8,9] and is undoubtedly due to the promotion of a chain reaction, in the course of which the peroxide or some other intermediate adds temporarily to one end of the double bond. This is then blocked for the addition of one of the atoms in the hydrogen halide and the reaction is forced to take the unnatural course.

Another instance where the rates of reaction seem to change parallel to the heat content changes in a series of analogous reactions, is the substitution of bromine in hydrocarbons. Since the reaction may be looked upon formally as a dehydrogenation, followed by addition of hydrogen bromide, the calculations discussed on the previous pages may be again employed. It is thus readily found that the substitution of bromine in a primary position is accompanied by 10.5 kcal. heat evolution, substitution in the secondary one by 13.6 and that in the tertiary one by 16.0 kcal. The increasing heat evolution in this order is wholly paralleled by the well-known kinetic tendency of bromine to replace hydrogen on the most highly substituted carbon atom of a hydrocarbon molecule.

The opposite trends of the heats of hydrogenation and bromination, so prominent in the ethylenic series, must be limited to those molecules where the changes of the reaction heats are conditioned by the interactions of the addenda with the neighboring groups. In particular, a decrease in the heat of hydrogenation due to the existence of conjugation in a diene or some other conjugated system, must be paralleled by a similar decrease of the heat of bromination, unless the now accepted theory of conjugation is incorrect and the phenomenon is not a stabilization of the double bond system by mutual interaction. There is thus offered, in the comparative study of the hydrogenation and the bromination heats, a more reliable and accurate method for a differentiation between conjugation energies and "steric" effects, than is possible from the analysis of the hydrogenation data alone; it is hoped to put this idea into practical form in the near future.

The failure to measure the heat of bromination of isobutene merits a brief comment. It has been known for some time[12] that upon addition of halogens to isobutene there is a tendency to form methallyl halide and free halogen acid. Under the conditions of bromination in the calorimeter this last reaction is thermodynamically possible, which conclusion is arrived at by comparison with the equilibrium between isobutene, hydrogen bromide and *t*-butyl bromide.[8] The noteworthy point is, however, that neither propylene nor trimethylethylene gives rise to such a reaction when brominated under *identical* conditions, although in at least one of these cases the equilibrium must be as favorable for decomposition of the dibromide as with isobutene. Thus purely kinetic factors of undetermined but highly specific nature must make the decomposition of the dibromide of isobutene occur exceptionally rapidly.

In concluding this discussion it may be pointed out that the difference of the heats of bromination of the *cis*- and *trans*-butenes-2 is quite close to the difference in their heats of hydrogenation. In the latter of these reactions the same end product is obtained, but the bromination of *cis*-butene-2 leads to the *dl*-mixture, while *trans* gives the *meso* form of the dibromide.[4] It is therefore evident that the heat content difference of these two compounds is quite small, if not zero.

Acknowledgment.—The late Professor E. P. Kohler has given us, as usual, much helpful ad-

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[11] Ogg and Polanyi, *Trans. Faraday Soc.*, **31**, 482 (1935); Gershinowitz, *J. Chem. Phys.*, **4**, 363 (1936).

[12] Pogorshelski, *J. Russ. Phys.-Chem. Soc.*, **36**, 1129, 1486 (1905); Linnemann and Zotta, *Ann.*, **162**, 36 (1872).

vice and we are also grateful to Dr. J. B. Conant for his valuable suggestions. Dr. W. E. Vaughan and Dr. Ralph D. Thompson have taken part in the early stages of this work.

Summary

Certain brominations and chlorinations have been studied calorimetrically, the following being the results

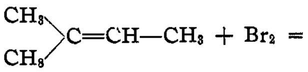
$$C_2H_4 + Br_2 = C_2H_4Br_2 - 29{,}058 \pm 300 \text{ cal.}$$

$$C_3H_6 + Br_2 = C_3H_6Br_2 - 29{,}412 \pm 200 \text{ cal.}$$

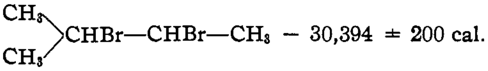
$$H_2C{=}CH{-}C_2H_5 + Br_2 = CH_2Br{-}CH_2Br{-}C_2H_5 - 29{,}585 \pm 200 \text{ cal.}$$

$$\textit{trans-}H_3C{-}CH{=}CH{-}CH_3 + Br_2 = \textit{i-}CH_3{-}CHBr{-}CHBr{-}CH_3 - 29{,}075 \pm 200 \text{ cal.}$$

$$\textit{cis-}H_3C{-}CH{=}CH{-}CH_3 + Br_2 = \textit{dl-}CH_3{-}CHBr{-}CHBr{-}CH_3 - 30{,}177 \pm 200 \text{ cal.}$$



$$(CH_3)_2C{=}CH{-}CH_3 + Br_2 =$$



$$(CH_3)_2CHBr{-}CHBr{-}CH_3 - 30{,}394 \pm 200 \text{ cal.}$$

$$C_2H_4 + Cl_2 = C_2H_4Cl_2 - 43{,}653 \pm 120 \text{ cal.}$$

All heats of reaction refer to 355°K. and gases at one atmosphere total pressure.

The most notable conclusion to be drawn from these data is that substitution on the ethylenic group results in increased heat evolution on addition of bromine, while previously it was found to decrease the heat of hydrogenation.

It is pointed out that the observed trends give a thermodynamic basis to the so-called Markownikoff rule and to the trend of bromine to replace hydrogen on the most substituted carbon atom of a saturated hydrocarbon. A rule is formulated which makes possible a calculation of quite accurate heats of addition of hydrogen halides and of substitution of bromine.

CAMBRIDGE, MASS. RECEIVED AUGUST 5, 1938

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, WILLIAMS COLLEGE]

The Solubility of Carbon Dioxide in Deuterium Oxide at 25°[1]

BY JAMES CURRY AND C. L. HAZELTON

In the course of measuring the first ionization constant of deuterio-carbonic acid, it was found necessary to determine the solubility of carbon dioxide in deuterium oxide. This measurement is of interest in itself since, up until the present, no values for the solubility of gases in deuterium oxide have appeared in the literature.

Experimental

Apparatus.—The apparatus used was of the Ostwald type[2] and the measurements were carried out by means of the "dry method." The buret, which was surrounded by a water jacket, had a volume of 10 cc. and was graduated in 0.05 cc. The absorption vessel had a volume of approximately 7 cc. The buret and the absorption vessel were connected by a flexible piece of copper tubing 1.5 meters long and 1 mm. internal diameter. In order to fasten the copper tubing to the glass, short pieces of 7-mm. glass tubing were sealed to the three-way capillary stopcocks which were at the top of the buret and the absorption vessel. The copper tubing was inserted to a depth of about 3 cm. into the glass tubing and the joints were then made fast with picein. In order to minimize breakage the copper tubing was held by a brass clamp at a point near the picein joint at the buret stopcock. This clamp in turn was fastened to the ringstand which held the buret. Another type of brass clamp, acting as a splint, strengthened the other copper–picein–glass joint at the absorption vessel. This mode of connection permitted a vigorous shaking of the absorption vessel but when necessary it was very simple to disconnect the latter.

Materials.—The carbon dioxide came from a commercial tank. It was analyzed by absorption in a potassium hydroxide solution and was found to be 99.8% pure.

The deuterium oxide was from a commercial source and at the beginning of the measurements was 99.9% D_2O. It was purified by distillation from alkaline permanganate, then from phosphoric anhydride and finally carried through a distillation without any reagents in a still especially reserved for this purpose. Before use the deuterium oxide was refluxed in order to remove any dissolved gases. During this operation it was protected from the atmosphere by means of a soda lime–calcium chloride tube. After the solubility measurements were completed the deuterium oxide was used for ionization constant determinations and when these were finished the analysis was 99.1% D_2O.

Measurements.—These were carried out in the usual manner except that a few slight modifications were necessary because the quantities of deuterium oxide used were relatively small and deuterium oxide is hygroscopic. During a measurement the absorption vessel was shaken in a thermostat adjusted to 25.00 ± 0.01°. The absorption vessel contained a short piece of 1-mm. copper wire which moved about during the shaking and thus aided in

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[1] Based on a thesis presented by C. L. Hazelton to Williams College in 1938, in partial fulfilment of the requirements for the degree of Master of Arts.

[2] Just, *Z. physik. Chem.*, **37**, 342 (1901).