resents our best present estimate of the conditions under which the reaction becomes explosive; data given in the figure may be used in conjunction with equation (1) in designing apparatus and determining suitable conditions for the smooth, non-explosive oxidation of phosphorus tribromide.

In addition to the results summarized in Fig. 1, other evidence bearing on the mechanism of the reaction may be drawn from our data. It appears that the oxidation of phosphorus tribromide (to oxybromide) is catalyzed by nitrogen tetroxide but not by nitrogen dioxide. Even at high temperatures and fairly high nitrogen dioxide pressures the non-explosive oxidation goes only slowly when little or no tetroxide is present. Under these conditions induction periods ranging from 140 to 1100 seconds were observed. When the velocity constants were plotted against temperature (Fig. 1) the points representing different nitrogen tetroxide pressures fell on regularly spaced isobars; the points representing different nitrogen dioxide pressures did not seem to fit into any pattern. The rate of the mild oxidation is thus more or less independent of the nitrogen dioxide pressure; at high temperatures and high nitrogen dioxide pressures, of course, other reactions involving the dioxide do take place. Further analysis of the curves in Fig. 1 indicates that at constant temperature, at least up to 100°, the velocity constants are directly proportional to the nitrogen tetroxide pressures. The oxybromide probably acts only as a diluent, except above the temperature at which dissociation begins.

Apparatus and materials used in this work were purchased with a grant from the Alexander Dallas Bache Fund of the National Academy of Sciences.

## Summary

Over a limited range of conditions, in the presence of nitrogen oxides and oxygen, phosphorus tribromide vapor is oxidized rapidly yet non-explosively to the oxybromide. The effect of various factors on the velocity of the oxidation has been studied, and the conditions under which the reaction can be controlled have been outlined.

AUSTIN, TEXAS RECEIVED AUGUST 22, 1940

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

# Heats of Organic Reactions. X. Heats of Bromination of Cyclic Olefins

BY M. W. LISTER[1]

Studies of the heats of hydrogenation and bromination of unsaturated organic compounds published in recent years from this Laboratory[2] have established certain regular relations between these quantities and the structures of the molecules investigated. The previous work was limited to gas phase reactions, and the study of brominations in particular was confined to the simplest molecules because of the low vapor pressures of the products. The present experiments are an extension to reactions in the liquid phase. The brominations of a series of cyclic olefins have been investigated, and the results throw further light on the causes of the regularities previously noted.

## Experimental

The calorimeter was designed for general utility in measuring heat changes in liquid phase reactions. It is an improvement on an apparatus developed by R. B. Williams in this Laboratory but not yet described in the literature.

It consisted of a long-necked spherical Dewar flask of 500-cc. capacity, with the bottom of the inside of the neck ground into a conical joint. Into this fitted a platinum cup from which tubes, closed at the bottom and open at the top, dipped into the body of the flask. These contained (i) a platinum resistance thermometer, (ii) a constantan wire resistance, both occupying only lower parts of the tubes so that they were completely below the level of the liquid in the flask. A brass cup was soldered into the platinum cup to strengthen it. The leads to the thermometer and to the resistance were brought out through thin stainless steel tubes, soldered into the brass cup. This design ensured (i) low heat exchange with the outside, (ii) that no vapor from the liquid in the flask could diffuse into the neck, and there condense.

In order that the reaction to be measured could be started at any given time, one of the reagents (usually bromine) was placed in a sealed glass ampoule which could be broken during the operation of the calorimeter. This ampoule was held in a platinum basket slung from hooks on the underside of the platinum cup, and was broken by striking down a thin platinum rod fitting closely in a stainless steel tube soldered to a short and narrow platinum

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[1] Commonwealth Fellow.

[2] Kistiakowsky, *et al.*, THIS JOURNAL, **61**, 1868 (1939), and earlier.

tube projecting upward from the platinum cup. The reactions could thus be carried out so that the materials came into contact with only glass and platinum. The calorimeter was held suspended in a water thermostat by a brass frame, and its contents were stirred continuously by oscillating the whole flask round an axis just above the top of the neck. The metal parts of the ground joint were held in place by a spring and lubricated with phosphoric acid grease.

The constantan wire resistance was used to determine the electrical energy equivalent of the flask and its contents, by observation of the temperature change associated with a measured quantity of electrical energy. To determine the latter, four-wire connection was used; the potential across a 1-ohm standard resistance in series with the resistance wire was measured to give the current, and a standard fraction, from a potential divider, of the potential across the resistance was measured to give the voltage. A Queens type potentiometer was used for these purposes.

The temperature changes in the calorimeter were followed with a platinum resistance thermometer (about 22 ohms at 25°), and a Mueller type bridge. The bridge was maintained at constant temperature in an air thermostat, and was capable of measuring down to 0.0001 ohm (or 0.0012° on the platinum thermometer). It was found that the heat capacity of the calorimeter (containing carbon tetrachloride), as determined by these electrical measurements, did not depend on the rate of heating. The following is the result of a typical test run.

| Energy input in cal./min.[a] | Energy equivalent (cal./deg.) |
|---|---|
| 34.40 | 167.5 |
| 118.25 | 167.7 |
| 22.14 | 168.25 |

[a] Calorie is here defined as 4.1833 Int. Joules.

The slight drift is due to progressive warming of the carbon tetrachloride, and consequent rise in its heat capacity.

## Experimental Procedure

The reactions investigated were additions of bromine to various olefins. The flask was filled with about 450 cc. of a carbon tetrachloride solution of the olefin. Carbon tetrachloride was carefully purified before use. The ampoules to be broken contained a weighed amount, usually 3 to 4 g., of redistilled bromine, while the hydrocarbon was always present in about threefold excess. At the end of a run a test was made for free bromine and for hydrogen bromide, but neither was ever found. Two determinations of the heat capacity of the flask and reaction mixture were made during each run, one before and one after reaction. Warming or cooling rates of the liquid were observed before and after reaction or electrical heating, and the temperature changes associated with these were corrected by linear extrapolation of the rates.

The heats of solution of the olefins and their dibromides in carbon tetrachloride were measured directly by breaking an ampoule of about 1-cc. capacity of the compounds into carbon tetrachloride in the calorimeter. The heat changes thus observed were small, usually less than 0.0003 ohm (equivalent to about 100 cal./g. mole) in the platinum resistance thermometer.

The results are given in Table I. After the heat of each reaction is given first the average deviation from the mean, and then in parentheses the number of experiments. The heat of solution figures are all the means of two experiments. These values apply to carbon tetrachloride solution at 27°.

TABLE I

| Reaction | Heat of reaction in solution (cal./mole) $-\Delta H_{300}°$ | Heat of solution in $CCl_4$: $-\Delta H_{300}°$ olefin | dibromide |
|---|---|---|---|
| Cyclopentene + $Br_2$ | 25789 ± 59 (2) | 274 | 36 |
| Cyclohexene + $Br_2$ | 30448 ± 124 (6) | 209 | 36 |
| Cycloheptene + $Br_2$ | 27256 ± 36 (2) | − 24 | 33 |
| Cycloöctene + $Br_2$ | 24949 ± 147 (2) | 70 | −271 |
| *n*-Heptene-1 + $Br_2$ | 27194 ± 152 (4) | − 84 | 55 |
| *n*-Butene-1 + $Br_2$ | 26921 ± 276 (3) | | − 99 |

**Vapor Pressure Determinations.**—To convert these results to the gas phase it is necessary to know the heats of vaporization of the compounds involved. These were obtained from vapor pressure measurements on a static apparatus shortly to be described by Kistiakowsky, Conn and Roberts, which utilizes a supersensitive quartz spiral for pressure measurements. The sensitivity of the manometer is better than 1 micron and the reproducibility of readings is about 4 microns. The pressures were generally in the range 0.1 mm. to 100 mm., and gave heats of vaporization differing considerably from those calculated from Trouton's rule, which indicated a fairly large temperature variation of these quantities. The vapor pressures were usually measured over a range of temperatures, whose midpoint differed from the reaction temperature, 27°. To correct the observed values to 27°, a temperature gradient for these heats of vaporization was used calculated on the assumption that the entropy of vaporization varies linearly with log $p$, and has values 21 at 760 mm., and 33 at 10 mm. (the value 33 is the mean obtained from the present observations). This assumption allows a heat of vaporization to be calculated from any one vapor pressure, and the values so obtained were generally not in accurate agreement with experiment, but the correction so obtained can not have been much in error because of the short range of extrapolation. Table II gives the results, and the heats of vaporization corrected to 27°.

The heat of vaporization of bromine was calculated from vapor pressure data in "I. C. T." Values of this quantity were calculated from each successive pair of pressures observed, and the best line drawn through these values plotted against temperature. The figure so obtained for 27° was 7466 cal.

**Preparation of Materials.**—All the hydrocarbons used, except heptene-1, were parts of specimens prepared by Kistiakowsky and co-workers, when working on heats of hydrogenation. Heptene-1 was prepared by the method given by Kistiakowsky, Ruhoff, Smith and Vaughan.[3] The refractive index and boiling point of the product agreed with their values. Specimens of the dibromides were obtained from bromine and the olefins in a suitable solvent, usually carbon tetrachloride, and purified by frac-

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[3] Kistiakowsky, Ruhoff, Smith and Vaughan, THIS JOURNAL, 58, 137 (1936).

TABLE II

| Compound | T, °C. | $P_{mm.}$ | Ht. of vaporization at 27°, $\Delta H$, cal. |
|---|---|---|---|
| Cyclopentene | −42.75 | 10.85 | 6780 |
| | −24.18 | 35.37 | |
| | 0 | 129.7 | |
| | 19.77 | 299.2 | |
| Cyclohexene | −44.42 | 1.20 | 7789 |
| | −24.85 | 5.64 | |
| | 0 | 25.09 | |
| | 18.45 | 65.43 | |
| Cycloheptene | −21.44 | 1.41 | 8779 |
| | 0 | 6.16 | |
| | 19.82 | 19.77 | |
| | 39.06 | 49.31 | |
| Cycloöctene | 0 | 1.57 | 9936 |
| | 19.83 | 5.81 | |
| | 40.36 | 17.50 | |
| | 60.22 | 44.61 | |
| Heptene-1 | −17.69 | 4.63 | 8587 |
| | 0 | 14.71 | |
| | 19.26 | 42.60 | |
| | 39.09 | 107.9 | |
| Cyclopentene dibromide | 0 | 0.179 | 11428 |
| | 19.49 | .741 | |
| | 41.26 | 2.97 | |
| | 59.04 | 7.48 | |
| Cyclohexene dibromide | 0 | 0.036 | 12069 |
| | 17.76 | .146 | |
| | 39.81 | .573 | |
| | 59.45 | 1.89 | |
| Cycloheptene dibromide | 19.75 | 0.113 | 12432 |
| | 39.94 | .425 | |
| | 59.54 | 1.27 | |
| | 79.67 | 3.84 | |
| Cycloöctene dibromide | 19.97 | 0.060 | 13036 |
| | 40.27 | .205 | |
| | 59.65 | .664 | |
| | 80.10 | 2.00 | |
| 1,2-Dibromoheptane | 22.07 | 0.126 | 13005 |
| | 40.45 | .497 | |
| | 59.80 | 1.50 | |
| | 79.85 | 4.37 | |
| 1,2-Dibromobutane | 0 | 0.548 | 10801 |
| | 19.65 | 2.18 | |
| | 39.75 | 7.26 | |
| | 59.86 | 20.37 | |

tional distillation. They consisted of colorless oils with the following refractive indices.

| Compound | $n^{24}$ |
|---|---|
| Cyclopentene dibromide | 1.5444 |
| Cyclohexene dibromide | 1.5521 |
| Cycloheptene dibromide | 1.5544 |
| Cycloöctene dibromide | 1.5542 |
| 1,2-Dibromoheptane | 1.4983 |

**Discussion of Errors.**—As five measurements, namely, those of the heat of reaction in solution, two heats of solution and two heats of vaporization, were necessary to give one heat of reaction in the vapor phase the final probable error was relatively large. If we take first the heat of reaction in solution, the values obtained from various experiments spread in the worst case over a range of rather more than 1%, while the worst average deviation from the mean, excluding butene-1, was 0.6%. Besides this random error, various sources of systematic error may have been operative, though these were as far as possible tested for or guarded against. Tests were always made for unreacted bromine, and for hydrogen bromide from possible substitution reactions, but these were never found. In the calculation of the results linear extrapolations of the observed cooling (or warming) rates were used, but the error in this assumption must have been small, since the heat exchange with the outside gave a temperature drift of only one-six-hundredth of the difference between the flask temperature and its equilibrium temperature per minute, and the time of extrapolation was less than twenty minutes, usually much less.

As a check on the operation of the calorimeter, two measurements were made of the reaction, $KOH + HCl \longrightarrow KCl + H_2O$, with 14 $N$ acid in the ampoule and 0.035 $N$ alkali in the flask. The heat of dilution of the strong acid to $N/50$ acid was also measured, and the results converted to infinite dilution by means of Rossini's data[4] and compared with previous values of the reaction $H^+ + OH^- \longrightarrow H_2O$ at infinite dilution and a temperature of 25°. One run gave a value 26 cal. above previous measurement, and other 158 cal. low. Thus the average deviation (92 cal.) is too small to indicate the presence of systematic errors. It is estimated that ±300 cal. (or 1%) is a liberal figure for the error in the liquid phase reaction measurements.

One would expect that the heats of mixing of carbon tetrachloride with the various olefins and their dibromides would be small, and in the majority of cases the observed value was less than 100 cal. Where the value was not virtually zero, it seemed possible that the deviation was due to such causes as a trace of polymerization or of dissociation (in cycloöctene dibromide). Finally it seemed best to take these heats of mixing as zero, but to allow an extra experimental error of ±1% from this cause.

(4) Bichowsky and Rossini, "Thermochemistry," Reinhold Publishing Corp., New York, N. Y., 1936.

The chief source of doubt in the determination of the heats of vaporization was the uncertain magnitude of the temperature gradient of this quantity, though the method used to correct the results to 27° cannot be much in error. In the majority of cases very good plots of log $p$ against $1/T$ showed that random errors could not be very great. The range over which measurements were made was 60°, and this could not have been much extended without encountering rather high vapor pressures (introducing errors due to deviation from perfect gas laws or decomposition). An accuracy of ±3% (about 300 cal.) can reasonably be claimed for the heats of vaporization.

The final figure for the reaction converted to the gas phase is thus probably accurate to ±600 cal. as a conservative estimate.

TABLE III

| Gaseous reaction | $-\Delta H$ cal./mole at 27° |
|---|---|
| Cyclopentene + $Br_2 \longrightarrow C_5H_8Br_2$ | 28610 |
| Cyclohexene + $Br_2 \longrightarrow C_6H_{10}Br_2$ | 33630 |
| Cycloheptene + $Br_2 \longrightarrow C_7H_{12}Br_2$ | 30440 |
| Cycloöctene + $Br_2 \longrightarrow C_8H_{14}Br_2$ | 29310 |
| *n*-Heptene-1 + $Br_2 \longrightarrow C_7H_{14}Br_2$ | 30240 |
| Butene-1 + $Br_2 \longrightarrow C_4H_8Br_2$ | 28900 |

**Discussion of Results.**—The values obtained for the heats of bromination converted to the gas phase at 27° are given in Table III. The value for butene-1 is in fair agreement with that found by Conn, Kistiakowsky and Smith[5] for this reaction at 82°, namely, 29756 cal., but it may be a little low because of possible evaporation of butene from the solution. For a reaction of this sort, $-\Delta H$ would be expected to decrease with falling temperature, though not by as much as the comparison of these figures suggests, but the residual difference is within the experimental error. Because of experimental errors little significance can be attached to the higher heat of bromination of *n*-heptene-1 than of butene-1, though it seems possible that this difference is real, even if small.

Any theory proposed to explain the results of Table III should, to be satisfactory, be capable also of explaining the heats of addition of hydrogen and bromine to various olefins, reported by Kistiakowsky and co-workers. They found that the heats of hydrogenation of acyclic olefins fell into groups determined by the number of carbon atoms directly linked to the atoms forming the double bond, and that an increase in this number lowered the heat of hydrogenation. The heats of bromination on the other hand varied in the opposite direction, though the differences were much smaller. Cyclic olefins showed the greatest heat of hydrogenation in cyclohexene, where the value was almost the same as for *cis*-butene-2; for cyclopentene and cycloheptene the figures were lower and roughly equal, and for cycloöctene lower still. They are given in Table IV.

TABLE IV

| Olefin | Heat of hydrogenation (82°) ($-\Delta H$) cal./mole |
|---|---|
| Cyclopentene | 26915 |
| Cyclohexene | 28592 |
| Cycloheptene | 26386 |
| Cycloöctene | 23525 |

The trends of these results resemble those for bromination qualitatively, even if not quantitatively.

The most probable explanation, at least at first sight, of these variations, is that a considerable interaction energy exists between the atoms or groups attached to two bonded carbon atoms. Spectroscopic and heat capacity data (on such compounds as ethane, propane, etc.) leave no doubt that an interaction is present, and of such a nature as partially to restrict rotation round the C–C single bond, but it remains to be shown, firstly, whether repulsions or attractions are involved, and, secondly, whether the present results can be explained on the basis of these interactions alone.

Langseth, Bernstein and Bak[6] claim to have deduced from Raman spectra that the carbon atoms in cyclohexane form a plane regular hexagon, and that various halogen substituted ethanes take up opposed rather than staggered configurations. They therefore suppose that an attractive force exists between the atoms concerned, a force which must be of considerable magnitude since it can distort the carbon valency angles in cyclohexane to 120°.

An opposite conclusion has been reached from the studies of electron diffraction by various hydrocarbon vapors,[7] and by ethylene dihalides.[8] A non-planar configuration was assigned to cyclohexane, and the halogen atoms in the dihalides were given positions as far apart as possible.

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(5) Conn, Kistiakowsky and Smith, THIS JOURNAL, **60**, 2764 (1938).

(6) Langseth, Bernstein and Bak, *J. Chem. Phys.*, **8**, 410, 415 (1940).

(7) Pauling and Brockway, THIS JOURNAL, **59**, 1223 (1937).

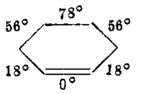
(8) Beach and Turkevich, *ibid.*, **61**, 303 (1939).

The heats of hydrogenation and bromination of olefins also provide evidence as to the relative merits of the "repulsion" or "attraction" theory, as they may be called for briefness. As will be seen in the following, neither provides a wholly satisfactory explanation of the observed heats of reaction, but the repulsion theory involves fewer inconsistencies and predicts qualitatively the observed trends.

Firstly, the heats of hydrogenation of *cis*- and *trans*-butene-2 show that the *cis* isomer is the more unstable by 949 cal. The potential barriers to free rotation, deduced spectroscopically, increase in going from ethane to propane to isobutane. This suggests that the carbon–carbon interaction exceeds the carbon–hydrogen or hydrogen–hydrogen interaction. If this is so, the interaction must be a repulsion in order that *cis*-butene-2 should be less stable than *trans*-butene-2.

The general tendency of progressive substitution of methyl groups for hydrogen to give lower heats of hydrogenation is explained on the repulsion theory if we assume the C–C repulsion to be more important than the C–H or H–H repulsions and to be greater in the paraffin than in the olefin. The latter proposition is made reasonable by a consideration of the distances between the carbon atoms concerned: 2.57 Å. in the planar *cis* position $^{\mathrm{C}}\diagdown_{\mathrm{C-C}}\diagup^{\mathrm{C}}$ and 2.94 Å. if this group takes up the staggered position with an angle of 60° between the planes of the $^{\mathrm{C}}\diagdown_{\mathrm{C-C}}$ and $_{\mathrm{C-C}}\diagup^{\mathrm{C}}$ groups; and 3.11 Å. in $^{\mathrm{C}}\diagdown_{\mathrm{C=C}}\diagup^{\mathrm{C}}$, if the $_{\mathrm{C=C}}\diagup^{\mathrm{C}}$ angle is taken as 125°. The results of bromination require the assumption that the Br–H repulsion slightly exceeds the Br–$CH_3$ repulsion. Conversely on the attraction theory we must suppose a smaller carbon–carbon attraction in the paraffin than in the olefin, or that hydrogen–hydrogen attractions are most important.

Though these results favor the repulsion theory, the evidence is not very strong, but the behavior of the series of cyclic olefins, cyclopentene to cycloöctene, provides much stronger reasons to adopt the repulsion theory.



Cyclopentene and cyclopentane, having planar rings, will contain high repulsion energies, since their configuration is entirely the "opposed" one. The most stable configuration of cyclohexene is probably that shown, the numbers giving the angles between the planes containing the pair of linked carbon atoms and first one and then the other of their two neighbors. This form will contain appreciable repulsive energy. Cyclohexane, on the other hand, has in its "chair" form all these angles equal to 60°, or an ideally staggered configuration so that it will contain little repulsive energy. Thus the heat of hydrogenation or of bromination will be more than for cyclopentene. In cycloheptene, however, the greater flexibility of the 7-ring will slightly decrease the repulsion energy in the olefin, but cycloheptene will be so puckered that each $^{\mathrm{C}}\diagdown_{\mathrm{C-C}}\diagup^{\mathrm{C}}$ group is twisted through more than 60°, giving a rather higher repulsion energy than in cyclohexane. These changes will decrease the heats of bromination or hydrogenation. For cycloöctene and cycloöctane, these effects are carried further, at least in the paraffin, where the general "twist" of $^{\mathrm{C}}\diagdown_{\mathrm{C-C}}\diagup^{\mathrm{C}}$ groups round the ring is about 110° or nearly opposed again, so that considerable repulsion energy should be present and the heats of addition lower still. It is possible that this opposed configuration constitutes part of the difficulty in forming 8-rings (and similarly for 9- or 10-rings) relative to 6-rings, while in much larger rings the regular arrangements are again staggered, with $^{\mathrm{C}}\diagdown\mathrm{C{-}C}\diagdown_{\mathrm{C}}$ groups twisted through nearly 180°, so that they are easier to form. It is readily seen that the attraction theory predicts precisely opposite trends, with cyclohexene giving the lowest heats of addition, though allowance must be made for the fact that the configurations to be expected for these molecules would be somewhat different from those given by the repulsion theory.

Thus in general the repulsion theory predicts correctly the qualitative trends, especially the similar behavior of the cycloölefins on hydrogenation and bromination, but the attraction theory does not. However, even on the repulsion theory the results do not show as high a degree of quantitative consistency as might be desired. A crude quantitative application of the theory can be attempted as follows. Let $E_{\mathrm{xy}}.f(\theta)$ be the repulsion energy between the atoms x and y in the group $^{\mathrm{x}}\diagdown_{\mathrm{C-C}}\diagup^{\mathrm{y}}$, when the planes containing the atoms $^{\mathrm{x}}\diagdown_{\mathrm{C-C}}$ and $_{\mathrm{C-C}}\diagup^{\mathrm{y}}$ cut at an angle $\theta$. In the *trans* planar form, $\theta$ is taken as 180°. Let $E^{*}_{\mathrm{xy}}.f(\theta)$ be the corresponding quantity in the group $^{\mathrm{x}}\diagdown_{\mathrm{C=C}}\diagup^{\mathrm{y}}$. We can suppose $E_{\mathrm{xy}}$ and $E^{*}_{\mathrm{xy}}$

to be independent of $\theta$, and $f(\theta)$ to be the same for all pairs of atoms x and y. The exact form of $f(\theta)$ is not known, but it will have a maximum at 0° and a minimum at 180°. The observed heat of reaction is then taken as made up of (i) the heat of addition $(-\Delta H_0)$ of bromine or hydrogen to an ideally isolated double bond to give an ideally isolated single bond, and (ii) of the difference between the repulsion energies in the products and the reagents.

Then for the reaction, $C_2H_4 + H_2 \longrightarrow C_2H_6$

$$-\Delta H = -\Delta H_0 + 2E^*_{HH}(f(0°) + f(180°)) - 6E_{HH}\,f(60°) - 3E_{HH}\,f(180°) = 32824 \text{ cal.}$$

A staggered configuration is assumed for ethane. Similarly for propylene ⟶ propane

$$-\Delta H = -\Delta H_0 + (E^*_{HH} + E^*_{CH})(f(0°) + f(180°)) - (E_{CH} + 2E_{HH})(2f(60°) + f(180°)) = 30115 \text{ cal.}$$

and so on for the butenes, tri- and tetramethylethylenes. Now if we subtract these equations in suitable pairs we get discordant values for the same quantity.

(i) $(E^*_{HH} - E^*_{CH})(f(0°) + f(180°)) + (E_{CH} - E_{HH})\text{-}(2f(60°) + f(180°))$
= 2709 cal. from ethylene and propylene
= 1726 cal. from propylene and isopbutene

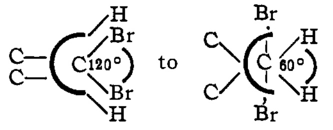
(ii) $(E^*_{CH} - E^*_{CC})(f(0°) + f(180°)) + E_{CC}(f(60°) + f(180°)) - E_{CH}\,f(180°) - E_{HH}f(60°)$
= 1469 cal. from isobutene and trimethylethylene
= 287 cal. from tri- and tetramethylethylene

The most that can be said is that the sign of these quantities is what would be expected, while on the attraction theory even this is not the case. The brominations of these olefins give no more consistent values.

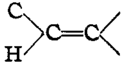
From the hydrogenations (converted to 27°) and brominations of the cyclic olefins, the heats of substitution of two bromine atoms in adjacent positions in cyclic paraffins can be obtained. Thus we have

$$C_5H_{10} + Br_2 \longrightarrow C_5H_8Br_2 + H_2 + 1942 \text{ cal.}$$
$$C_6H_{12} + Br_2 \longrightarrow C_6H_{10}Br_2 + H_2 + 5292 \text{ cal.}$$

The difference, 3350 cal., should represent the energy change in going from a configuration



The energy difference between two bromine atoms in completely *cis* and completely *trans*-positions would presumably be considerably larger. Beach and Turkevich[8] from electron diffraction data on ethylene dibromide deduce that this difference is greater than 5 kcal. but their conclusion is open to doubt since in arriving at it they assumed that the mutual energy of two bonded $CH_2Br$ groups has only one minimum, that of the *trans* configuration of the bromine atoms, and rises steadily to that of the *cis*-configuration.

A certain degree of inconsistency is found when the heats of hydrogenation and bromination of cyclohexene are compared. The heat of hydrogenation is nearly the same as that of *cis*-butene-2; this indicates that the repulsion energy in cyclohexene outside the group  $\mathrm{{}^{C}_{H}\!\!>\!C{=}C\!<\!{}^{C}_{H}}$ is the same as that in cyclohexane. The latter can assume a completely staggered configuration, so that its total repulsion energy should be small, which is not what would be expected of cyclohexene with its shape as indicated before. The heat of bromination of cyclohexene is 3.3 kcal. higher that that of *cis*-butene-2, a result which is more in line with the repulsion theory but which, on this simple theory, is incompatible with the heat of hydrogenation. Indeed a quantitative comparison of the heats of bromination and hydrogenation of these cyclic olefins suggests that the dibromides of even membered (*i. e.*, 6 and 8) rings possess, for some reason, extra stability.

The general conclusion must therefore be that while the repulsion theory gives a good qualitative account of these phenomena as opposed to the attraction theory, which does not, yet it is inadequate, at least in the simple treatment outlined above, to explain the results quantitatively. It is not certain at present what other factors are operative.

My thanks are due to Professor G. B. Kistiakowsky for his continued help throughout this work, and to the Commonwealth Fund for a Fellowship.

## Summary

A vacuum calorimeter for the study of reactions between volatile liquids is described. With its aid the heats of bromination of several cyclic and acyclic olefins have been measured in carbon tetrachloride solution. The vapor pressures of the olefins and of their dibromides were determined at several temperatures and from these the heats of vaporization calculated. Combination of these data led to calculation of the heats of bromination in the vapor phase. An

analysis of the latter data suggests that a theory which assumes repulsive forces between non-bonded adjacent atoms is much more consistent with experiments than a theory assuming attraction. However neither theory is capable, in a simple formulation, of accounting quantitatively for the observed changes in the heats of addition reactions.

MALLINCKRODT CHEMICAL LABORATORY
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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE RICE INSTITUTE]

# X-Ray Diffraction Studies in the System $CuO–Fe_2O_3$

BY W. O. MILLIGAN AND JAMES HOLMES

Cupric ferrite, $CuFe_2O_4$, has been synthesized by Holgersson[1] and by Wartmann and Thompson.[2] These investigators found it necessary to heat mixtures of cupric and ferric oxides to high temperatures, around 1000°. More recently Forestier and Longuet[3] reported that the gel prepared by adding sodium hydroxide to a mixture of cupric and ferric salts, and boiling for several hours, gave an X-ray diffraction pattern corresponding to cupric ferrite. Since this observation is inconsistent with the earlier work at high temperatures, and with the usual behavior of hydrous oxides upon aging,[4] further studies were made on this system. This paper reports the results of a systematic X-ray study of mixtures of varying composition of cupric and ferric oxides, precipitated at 25°, aged under water at 100°, and heated to 1000°.

## Experimental

**Preparation of Samples.**—A slight excess of sodium hydroxide was added dropwise to rapidly stirred mixtures of freshly prepared cupric and ferric chloride solutions[5] at 25°. The compositions of the chloride solutions were adjusted so that there was obtained a series of oxides containing 0, 10, 20, 30, 40, 50, 60, 70, 80, 90, and 100 mole per cent. (anhydrous basis) of cupric oxide. The precipitated gels were washed with distilled water, using a centrifuge, until the supernatant liquid was free of chloride ions, and air-dried at room temperature.

Portions of the air-dried samples were suspended in water at 100° for a period of twenty-four hours in a flask fitted with a reflux condenser, and air-dried at room temperature.

A second portion of each air-dried sample was heated for an hour at 1000° in a muffle furnace, quenched in cold water, and air-dried. A duplicate series of samples was prepared from nitrate solutions according to the directions of Wartmann and Thompson[2] and heated to 1000°.

**X-Ray Analysis.**—X-Ray diffraction patterns were obtained for the samples described above, using Mo $K_\alpha$ X-radiation. The results obtained for the original air-dried samples (Fig. 1), the samples aged at 100° (Fig. 2), and the samples heated to 1000° (Fig. 3) are given in the form of charts. The X-radiograms obtained for the samples prepared from the nitrate solutions are identical with those given in Fig. 3.

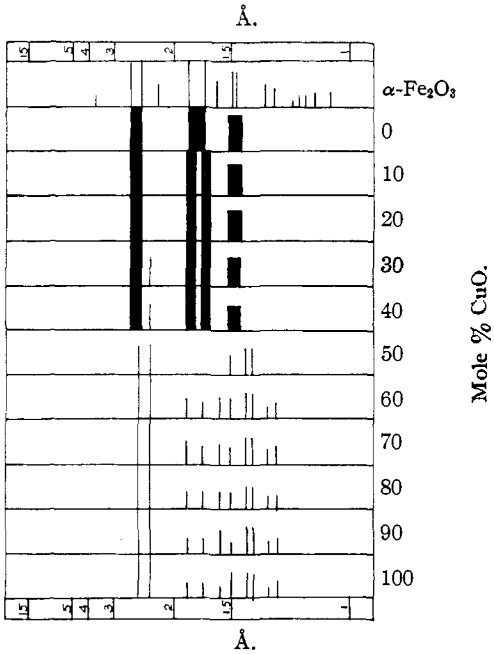

Fig. 1.—X-Ray diffraction diagrams for cupric and ferric oxides precipitated at 25°.

## Discussion

It is concluded from the X-radiograms of the original air-dried samples (Fig. 1) that there is no indication of the formation of cupric ferrite at 25°. The samples consist of mixtures of ferric oxide and cupric oxide. The pattern from the pure ferric oxide consists of a few broad bands, in

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(1) Holgersson, *Chem. Zentr.*, **100**, I, 372 (1929).

(2) Wartmann and Thompson, Bur. Mines, Dept. Investigations, No. 3228, p. 15 (1934).

(3) Forestier and Longuet, *Compt. rend.*, **208**, 1729 (1939).

(4) Weiser and Milligan, *Chem. Rev.*, **25**, 1 (1939); Weiser, "Inorganic Colloid Chemistry," Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1935.

(5) Old ferric chloride solutions may contain colloidal $\beta$-$Fe_2O_3 \cdot H_2O$; *cf.* Weiser and Milligan, THIS JOURNAL, **57**, 238 (1935).