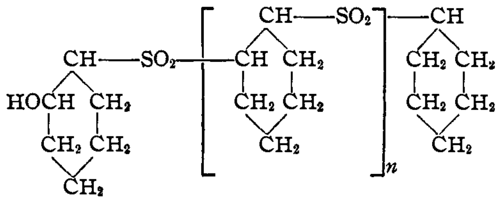
A considerable amount of sulfur containing organic material of the consistency of vaseline remained behind in the various alcohol extractions. Its composition was not determined.

Hydrolysis with 5% Sodium Hydroxide.—A mixture of 50 g. of the polymer and 140 cc. of 5% sodium hydroxide solution was heated under a reflux condenser on a steam-bath for about five days. Very little cyclohexene was produced. This solution was extracted with ether and the ether was evaporated. The residue was recrystallized from alcohol and melted at 138°. It contained sulfur; did not decolorize bromine in carbon tetrachloride solution; was not oxidized by alkaline potassium permanganate solution; and was insoluble in water, dilute acids or dilute alkalies. The analysis and molecular weight indicated that this product was dodecahydrophenoxthine dioxide.

Anal. Calcd. for $C_{12}H_{20}SO_3$: C, 59.02; H, 8.26; S, 13.1; mol. wt., 244. Found: C, 58.99; H, 8.24; S, 13.3; mol. wt. (cryoscopic in benzene), 236, 238.

Summary

1. It has been found that sulfur dioxide adds to cyclohexene in the presence of an oxidizing catalyst to produce a polymeric sulfone whose most probable structure is



2. Treatment of the polycyclohexene sulfone with chloroacetyl chloride yields a product containing halogen. Halogen analyses and molecular weight determinations indicate that the value of "*n*" is about thirty-nine, *i. e.*, the molecular weight is approximately 6000.

3. Isolation of octahydrodiphenyl, dicyclohexenyl sulfone, dodecahydrophenoxthine dioxide, cyclohexene, cyclohexenyl sulfinic or sulfonic acid and potassium sulfite from the alkaline decomposition of the polymer substantiate the above formula.

URBANA, ILLINOIS RECEIVED JUNE 20, 1934

COMMUNICATIONS TO THE EDITOR

IODINE CATIONS

Sir:

Philbrick [THIS JOURNAL, **56,** 1257 (1934)] and Faull and Baeckström [*ibid.*, **54,** 620 (1932)] have recently concluded that the number of iodine cations in a solution of iodine monochloride is negligible. It was demonstrated in 1920 [Howell and Noyes, THIS JOURNAL, **42,** 991 (1920)] that the iodine of a number of acetylene derivatives reacts in the positive form. It is true that we did not then recognize the sharp distinction between covalent and ionic linkages which Sidgwick has shown so conclusively in his Monograph ("Some Physical Properties of the Covalent Link in Chemistry," Cornell University Press, 1933), but the demonstration that iodine may react as a cation is still satisfactory. While very many reactions of chlorine and hypochlorous acid demonstrate the existence of chlorine cations, these cannot be shown by electrometric measurements [Noyes and Wilson, THIS JOURNAL, **44,** 1633 (1922)].

The iodine cation must have the structure, $:\ddot{\underset{\cdot\cdot}{I}}$. It has recently been pointed out [Noyes, *ibid.*, **55,** 658 (1933)] that while six-electron ions frequently take part in reactions the number of such ions is always small. The structure of several hundred thousand carbon compounds has been determined on the fundamental assumption that radicals are transferred from one compound to another in chemical reactions. The results are universally accepted in spite of the fact that only a very few of the radicals have been isolated. Similar methods may be used to advantage in determining the electronic structure of many compounds and radicals. The anion ICl_2^- is assumed in the papers referred to. This is possible only by assuming a coördination number of 5 for iodine, with six unshared electrons, $:\ddot{\underset{\cdot\cdot}{Cl}}\ \vdots\overset{-}{\underset{\cdot\cdot}{I}}\vdots\ \ddot{\underset{\cdot\cdot}{Cl}}:$, making the iodine negative, or that a chloride ion is held to the iodine atom by static attraction because of the positive dipole moment of the iodine monochloride. The latter appears more probable but the choice should be determined by x-ray measurements.

UNIVERSITY OF ILLINOIS WILLIAM A. NOYES
URBANA, ILLINOIS

RECEIVED JUNE 19, 1934

THE VAPOR PRESSURES OF HYDROGEN AND DEUTERIUM FLUORIDES

Sir:

The vapor pressures of several deuterium compounds have been measured before in this Laboratory and elsewhere.[1] Since the hydrogen bond has been regarded by Lewis as largely responsible for the differences in vapor pressures between the corresponding light and heavy compounds, it occurred to us that a comparison of the two hydrogen fluorides, in which this bond is particularly strong, would be interesting.

Two runs each with the light and heavy compounds were made as follows: hydrogen made from water and zinc dust at about 400° was pumped through a liquid air drier into a silver vessel containing silver fluoride made by the action of fluorine gas on its inner walls. This vessel was then heated to 110° until the pressure became constant. The hydrogen fluoride thus produced was frozen with liquid air, the residual hydrogen pumped off and distilled into a small copper cell, of total volume 6.3 cc., embedded in a large copper block. The block was surrounded by a cold alcohol-bath in a large Dewar vessel. The temperature rose about 1° per hour at the lower temperatures and 0.1° per hour at the higher. This system was closed off and the vapor pressure measured by means of a diaphragm gage,[2] and temperature by means of a three junction copper–constantan thermocouple.

The H^1F was made from 0.15 and 0.13 cc. of light water in the respective runs. The vapor pressure of H^1F between the pressures of 5 and 76 cm. of mercury is given by the equation

$$\log_{10} P_1 \text{ (cm.)} = 6.3739 - 1316.79/T$$

The average deviation of the points is 0.08°. All pressure readings were reduced to 0°. Our results differ by only 0.13° from those of Simons [THIS JOURNAL, **46,** 2179 (1924)] which lie within the accuracy of his measurements.

The two runs with H^2F were begun with 0.12 and 0.18 cc. of 99.5% H^2_2O kindly furnished us by Professor G. N. Lewis. The vapor pressures of the second sample came out slightly higher than the first and we give them the principal weight since the first sample would tend to clean H^1 out of the apparatus. The vapor pressure of H^2F is given by the equation

$$\log P_2 \text{ (cm.)} = 6.2026 - 1261.16/T$$

The average deviation is 0.07°.

The table gives vapor pressures of both forms at rounded temperatures.

T, °K.	H^1F, cm.	H^2F, cm.	P_2/P_1
240	7.71	8.87	1.150
250	12.78	14.39	1.126
260	20.38	22.49	1.104
270	31.40	34.01	1.083
280	46.89	49.95	1.065
290	68.11	71.42	1.049
Boiling points	293.07°	291.81°K.	Diff. = 1.26°

For comparison with other compounds, Fig. 1 is included.

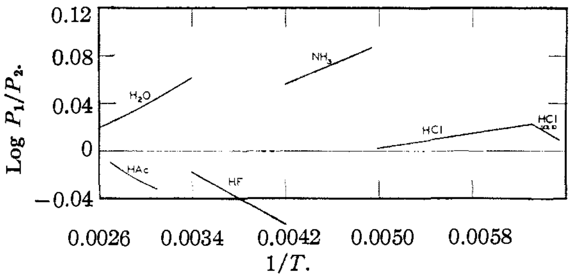


Fig. 1.

The deviation of the HF is in the same direction as with acetic acid but larger in magnitude. The most striking connection between acetic and hydrofluoric acids is that both are highly associated in the gas phase. It is evident that HF might lend itself to economic distillation at low pressure for the separation of the hydrogen isotopes. The heavy hydrogen would be removed, of course, at the top of the still, which would be very advantageous.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA

WILLIAM H. CLAUSSEN
J. H. HILDEBRAND

RECEIVED JULY 12, 1934

THE HYDROLYTIC FISSION OF AMINES

Sir:

In a recent paper, Kharasch and Howard [THIS JOURNAL, **56,** 1370 (1934)] suggest that the elimination of groups by hydrolytic fission from amines of suitable constitution is determined by the electronegative nature of the groups attached to the nitrogen.

It seems doubtful, however, whether this hypothesis can be extended to the other known examples of this type of reaction. Thus it has

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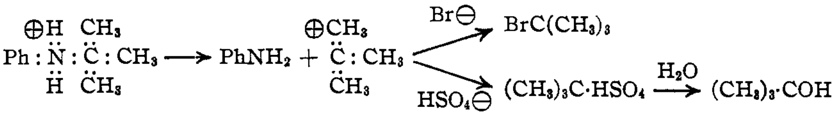
(1) H^2_2O, Lewis and Macdonald, THIS JOURNAL, **55,** 3057 (1933); H^2Cl, Lewis, Macdonald and Schutz, *ibid.*, **56,** 494 (1934); CH_3-$COOH^2$, Lewis and Schutz, *ibid.*, **56**, 493 (1934); H^2CN, Lewis and Schutz, *ibid.*, **56,** 1002 (1934); *cf.* also NH^2_3, Taylor and Jungers, *ibid.*, **55,** 5057 (1933).

(2) Claussen, *ibid.*, **56,** 614 (1934).

been found that *tert*-butylaniline and other alkylanilines containing *tertiary* alkyl groupings yield aniline on heating with aqueous mineral acids [Hickinbottom, *J. Chem. Soc.*, 1070 (1933); *Nature*, **131**, 762 (1933)]. Under precisely similar conditions, alkylanilines with *normal* alkyl groupings are unchanged. Further, diphenylamine or triphenylamine appears to be stable to hot mineral acid. Yet, according to Kharasch and Flenner [THIS JOURNAL, **54**, 681 (1932)] a *tertiary* alkyl group is less electronegative than the corresponding *normal* alkyl group and each is less electronegative than phenyl.

A more satisfactory basis for arriving at an explanation of such reactions appears to be the theory of chemical reactions developed by Lapworth and Robinson [Robinson, "Outline of an Electrochemical Theory of the Course of Organic Reactions," London, 1932; compare W. A. Noyes, THIS JOURNAL, **55**, 656 (1933)].

In *tert*-butylaniline, the induced effect of three methyl groups attached to a carbon atom is sufficiently intense to cause the transfer of an electron from the *tert*-butyl group to the nitrogen, provided that conditions are suitable and reagents are present to take advantage of this tendency. The hydrolysis of *tert*-butylaniline in acid solution is represented by the following scheme:



$$\mathrm{Ph}:\underset{\ddot{\mathrm{H}}}{\overset{\oplus\mathrm{H}}{\ddot{\mathrm{N}}}}:\underset{\ddot{\mathrm{C}}\mathrm{H_3}}{\overset{\mathrm{CH_3}}{\ddot{\mathrm{C}}}}:\mathrm{CH_3} \longrightarrow \mathrm{PhNH_2} + \underset{\ddot{\mathrm{C}}\mathrm{H_3}}{\overset{\oplus\mathrm{CH_3}}{\ddot{\mathrm{C}}}}:\mathrm{CH_3} \begin{cases} \xrightarrow{\mathrm{Br}\ominus} \mathrm{BrC(CH_3)_3} \\ \xrightarrow[\mathrm{HSO_4}\ominus]{} \mathrm{(CH_3)_3C{\cdot}HSO_4} \xrightarrow{\mathrm{H_2O}} \mathrm{(CH_3)_3{\cdot}COH} \end{cases}$$

The fate of the *tert*-butyl "ion" obviously depends on the experimental conditions. In concentrated hydriodic acid or hydrobromic acid, the corresponding *tert*-butyl halide is formed, while in more dilute solution increasing amounts of the carbinol result. This has been confirmed experimentally.

The hydrolysis of triphenylmethylaniline [Elbs, *Ber.*, **17**, 702 (1884); Hemilian, *ibid.*, p. 746; Gomberg, *ibid.*, **35**, 1829 (1902)] is represented similarly.

It is evident that, if the induced effect is enhanced by suitable substituents, the tendency to hydrolytic fission is also increased. Recorded examples of this are the elimination of nitrotoluidines from di- and tetranitro-di-*p*-tolylaminobutanes under the influence of hot diluted mineral acid [Morgan and Hickinbottom, *J. Soc. Chem. Ind.*, **43**, 307T (1924); compare Morgan, Hickinbottom and Barker, *Proc. Roy. Soc.*, **A110**, 518 (1926)]; the ready formation of aryl sulfonanilides from the aryl sulfonyl derivatives of *tert*-butylaniline by heating with diluted sulfuric acid.

The same theoretical considerations which have been used to explain the hydrolytic fission of *tert*-butylaniline and triphenylmethylaniline can be applied to account for the sensitivity of the *tert*-butyl halides and triphenylmethyl halides to hydrolysis.

THE UNIVERSITY
BIRMINGHAM, ENGLAND
WILFRED JOHN HICKINBOTTOM

RECEIVED JULY 18, 1934

THE EXCHANGE REACTION BETWEEN DEUTERIUM AND WATER VAPOR ON SURFACES

Sir:

We have observed a rapid conversion of deuterium to hydrogen on catalytic hydrogenating surfaces such as chromium oxide gel and zinc oxide which conversion may be ascribed to the deuterium-water exchange reaction. The existence of this exchange is important, since it may, under favorable circumstances, lead to the practically complete replacement of deuterium by the light isotope in a reaction mixture. In ordinary circumstances it can readily lead to the introduction of hydrogen into what may have been assumed to be pure deuterium.

We have analyzed by the thermal conductivity method of Farkas and Farkas [*Proc. Roy. Soc.* (London), **144A**, 467 (1934)] the gases desorbed by Dr. H. W. Kohlschuetter from a 15.5-g. sample of chromium oxide gel on which the velocity of activated adsorption of pure deuterium gas at 184° was being measured. In successive experiments, during each of which 25 cc. of pure deuterium was adsorbed, the desorbed gases analyzed, respectively, 98.5, 97.5, 92.5 and 87% of the *light isotope.* The adsorbent was then allowed to take up approximately 550 cc. of deuterium at about 350°, in units of 100 cc., the adsorption of each unit being followed by desorption at the same temperature. The gas desorbed from the surface after a further 25 cc. of deuterium had been adsorbed at 184°, in the manner of the first experiments recorded, now analyzed 41% light isotope, pointing to an exhaustion of the hydrogen source on the surface. The exchange was now repeated at 184° in the reverse direction. Hydrogen to the extent of 25 cc. was adsorbed and the desorbed gas then analyzed. It proved to be 45.5% hydrogen and 54.5 deuterium. The closeness of the analyses in successive experiments using first deuterium and then hydrogen points to the establishment of an equilibrium on the adsorbent surface best explained as an equilibrium between hydrogen, deuterium water and deuterowater, the water being present as a unit in the gel structure of the chromium oxide.

This conclusion is further confirmed by the observed influence of temperature on the reaction. At 0° the gas from a partially deuterized gel treated with deuterium for 12.5 hours showed only 11% hydrogen. This was not due to exhaustion of hydrogen from the surface, since, in succeeding experiments at 100°, samples of deuterium were converted to gas containing 47 and 51.5% of hydrogen, respectively, after nine and fifteen minutes of contact. The experiments of Gould, Bleakney and Taylor [*J. Chem. Phys.*, **2**, 362 (1934)] would lead one to expect a much more rapid interchange at 0° if the process involved only adsorbed hydrogen gas and deuterium.

Similar experiments with zinc oxide (*ex* oxalate), in the preparation of which no hydrogen gas was used, point also to water as the source of the hydrogen. Our experiments indicate a much more rapid exhaustion of the hydrogen source in this case than with the gel structure. Hydrogen production may be renewed on such exhausted surfaces on addition of water vapor. Platinized asbestos when first treated with deuterium also shows hydrogen formation, slower than on the gel and also exhausted by continued treatment with deuterium.

FRICK CHEMICAL LABORATORY
PRINCETON, N. J.
HUGH S. TAYLOR
H. DIAMOND

RECEIVED JULY 17, 1934

LIQUID-LIQUID EQUILIBRIA INVOLVING HEAVY WATER

Sir:

Since deuterium water is not so good a salt solvent as ordinary water [Taylor, Caley and Eyring, THIS JOURNAL, **55**, 4334 (1933)], we examined the effect of increasing deuterium content on the lower consolute temperature of nicotine and water and on the (upper) consolute temperature of phenol and water. As expected, the former was lowered and the latter raised as the deuterium content of the water increased. The amount of the lowering of the critical solution temperature of nicotine and water was for 3.9% D, 0.28°; and for 10.6% D, 0.72°. For phenol the corresponding increases were as follows: 3.89% D, 0.43°; 4.12%, 0.50°; 5.81%, 0.71°; 10.62%, 1.24°; 47.20%, 5.58°. The temperature increases in the case of phenol are linear in the % D so that an extrapolation to 100% D is possible. The indicated temperature rise is about 11.8°. No attempt was made to determine the extent of the H-D exchange in these experiments, but it is probable that the hydroxyl and amino hydrogen atoms exchanged completely while the rest did not. A single attempt to show a significant change in the isotopic composition of water as a result of consolution with phenol and subsequent unmixing was unsuccessful.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF WISCONSIN
MADISON, WISCONSIN
NORRIS F. HALL
HAROLD R. WENTZEL
THEODORE SMITH

RECEIVED JULY 16, 1934

OXYGEN ADDITION COMPOUNDS OF ACETYLENES

Sir:

We have recently found that many acetylenes acquire distinct oxidizing properties after coming in contact with air or oxygen. The acetylenes studied have been mainly of the types $RC\equiv CH$, $RC\equiv CR'$ and $RC\equiv CX$, where R and R′ represent alkyl and aryl groups, and X denotes a halogen. Although these acetylenes have been prepared by widely different methods, a large number of them upon exposure to air for several months contain almost the same amount of oxidizing agents. It is improbable, therefore, that the oxidizing properties of the acetylenes are caused by traces of olefins, for equal quantities of olefins would certainly not be formed by the various methods of preparation. It is conceivable that the acetylenes first polymerize, yielding olefinic derivatives which form peroxides. However, mono-alkyl and di-alkyl acetylenes contain very nearly the same amounts of peroxides after exposure to air for equal periods of time. Consequently, it is probable that the acetylenes themselves form peroxides. The similar concentrations of peroxide in many of the acetylenes may be due to a rearrangement of the peroxide into some more stable form when a certain definite concentration is reached. This hypothesis is supported by the ease with which the peroxides are destroyed by mild oxidizing agents.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF NOTRE DAME
NOTRE DAME, INDIANA
CHARLES A. YOUNG
R. R. VOGT
J. A. NIEUWLAND

RECEIVED JULY 25, 1934

OXYGEN ISOTOPE SEPARATION BY CHEMICAL REACTION

Sir:

A recent report by W. R. Smythe [*Phys. Rev.*, **45**, 299 (1934)] gives the $O^{16}:O^{18}$ ratio in oxygen obtained by the thermal decomposition of lead peroxide as 503 ± 10. He suggested that there might be some selectivity in the decomposition of the peroxide, favoring O^{16} and making his ratio too high. Since J. Krustinsons [*Z. Elektrochem.*, **40**, 247 (1934)] has recently shown that the decomposition of lead peroxide involves a series of solid solutions, there was a distinct possibility that isotope separation might in this case occur. Ordinarily, decomposition processes in solids occur only at interfaces between two phases and this limitation of reaction might well mask any selective reactivity of isotopes. We have, therefore, decomposed 450 g. of lead peroxide in a system which had been heated and evacuated at 235°. On raising the temperature to 270°, a sample of oxygen (I) was collected by means of a Sprengel pump. Four other samples were collected over a period of days and a final sample (VI) when the residual solid was practically all yellow in color, after a total decomposition time of sixteen days, the temperature having been raised slowly to 310°. An analysis of the first and last samples by Dr. W. Bleakney, of the Palmer Physics Laboratory, using the mass spectrograph, gave "uncorrected" ratios $O^{16}:O^{18}$ of (I) 468, 470, 472 and (VI) 470, 478, and 468. There is, therefore, no evidence at all of any fractionation of the isotopes. The data are in best agreement with measurements by Manian (Dissertations, Columbia University, 1934), using Bleakney's apparatus, on samples of oxygen from meteorites and potassium chlorate, and for which Manian finally arrived at a corrected abundance ratio of 514 ± 13, the correction (for scattered background) amounting to from 4 to 8%. Smythe's ratio does not differ from those of Manian nor our own.

We have also examined the oxygen released from 100 g. of "Superoxol," a 30% hydrogen peroxide, when treated, at ordinary temperatures, with colloidal platinum prepared by the Bredig method. The first sample (I) was that initially evolved, the last (II) was that remaining in the reaction vessel after completion of reaction and standing overnight. Comparative measurements by Dr. Bleakney under as closely comparable conditions as possible gave for the abundance ratio (uncorrected for scattered background) in these two samples: (I) 462 ± 8; (II) 426 ± 4. There appears, therefore, to be, in this case, a definite isotopic separation of oxygen, the divergence between the two analyses being far greater than anything hitherto found with oxygen analyses in the Bleakney mass spectrograph. The separation indicated is in the direction that would result from a less rapid release of O^{18} from the peroxide. We are extending these investigations to other modes of decomposition of hydrogen peroxide and to other materials yielding oxygen at low temperatures.

We wish to thank Dr. Bleakney for his assistance with the analyses.

FRICK CHEMICAL LABORATORY
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PRINCETON, NEW JERSEY
HUGH S. TAYLOR
AUSTIN J. GOULD

RECEIVED JULY 19, 1934