THE ENTROPY

Vol. 3 May 1957 No. 1

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ON THE COVER

Aloysius J. McGrail, Professor of Chemistry and Head of the Department of Chemistry at Providence College from 1931 until his death in 1945, received his undergraduate training at Harvard University and was graduated with the B.A. Degree in Chemistry in 1913. Continuing his studies, he received the Ph.D. Degree from Catholic University. After serving as an instructor of chemistry at Catholic University, he enlisted in the U.S. Army in the early days of World War I. He rapidly became an expert in the chemical aspects of military intelligence, engaging in some of the outstanding cases of the War.

Following a period of employment with the Ludlow Manufacturing Co. of Springfield, Massachusetts, Dr. McGrail joined the chemistry staff of Providence College in 1931. He immediately set out to revise the curriculum and to establish a Concentration in Chemistry, and was instrumental in the development of a more effective pre-medical department. He was responsible to a great degree, by his gifts and continued interest, for the early development of the science library.

Dr. McGrail was recalled to active duty in the preparative days of World War II with the rank of Lieutenant Colonel and served until his death in 1945.

Dr. McGrail will be remembered as an outstanding teacher, a willing
counsellor and a true and devoted friend of Providence College and her students. He was a man of pleasing yet at times stern disposition and took great joy in chiding the pre-medical students. His famous remark will be recalled by his many students: "Veterinarians are the only real doctors; horses can't tell you what's wrong with them".

Dr. McGrail will go down in the annals of Providence College as a man whose heart was in his work, the development of knowledge and character by his many students. The years have proven that his devoted effort was not in vain.

A bronze wall-plaque dedicating the organic chemistry laboratory in the Albertus Magnus Science Building to his memory has been recently installed.

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MOLECULAR ENERGY LEVELS

Dr. Cornelius Haas
Department of Chemistry, Brown University

According to quantum mechanics, a molecule can have definite amounts of energy; we say that the molecule has several energy levels. A transition between two energy levels can occur under the influence of electromagnetic radiation: a quantum \((hv)\) of light (frequency \(= v\)) provides the energy which enables the molecule to jump from level \(i\) (Energy \(E_i\)) to level \(j\) (Energy \(E_j\)); \(hv_{ji} = E_j - E_i\) (1). The molecule has absorbed one quantum of the light; thus the transition corresponds to light absorption. We will find an absorption band at frequency \(v\) where \(v\) is given by (1). Thus, if we measure the absorption spectrum and we plot transmission, \(T\), versus frequency, we will find an absorption band at the frequency \(v = \frac{T(E_j - E_i)}{h}\). Hence this absorption spectrum gives us information about the energy levels of the molecule.

We may distinguish various kinds of energy levels:

1. Electronic: The separation between electronic energy levels is greater than - 2. Vibrational: The separation between vibrational energy levels is greater than - 3. Rotational:

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(1) Edited from a Providence College Chemistry Colloquium, Nov. 13, 1956.
The separation between rotational energy levels.

We can understand this by a rough order of magnitude calculation. We will first calculate the order of magnitude of the electronic energy levels which involve the movements of the electrons. The forces between electrons are of the order of the coulomb interaction: \( e^2/r^2 \), where \( e = 4.8 \times 10^{-10} \) electron charge, and \( r = \text{distance} \approx 1\ A^0 = 10^{-8}\text{cm} \). Then, if \( f = e^2/r^2 = 25 \times 10^{-20}/10^{-16} = 25 \times 10^{-4} \) dynes, the apparent force constant (force/unit displacement) would equal \( 25 \times 10^{-4}\text{dyne}/10^{-8}\text{cm} = 25 \times 10^4\text{dyne/cm} \). The mass of the electron \( m = \frac{1}{1860} \times \frac{1}{1/6 \times 10^{23}} = 0.896 \times 10^{-27} \) gms. Hence the frequency of the motion will be about \( 1/2\pi (k/m)^{1/2} \) or \( v = 3 \times 10^{13} \text{sec}^{-1} \). If we express this frequency in terms of the wavelength of light with the same frequency we find that \( c/v = 3 \times 10^{10}/3 \times 10^{13} = 10^{-3}\text{cm} = 1000\ A^0 \). This means that we may expect electronic absorption bands in the ultraviolet (1000\ A^0), and eventually in the visible spectrum (5000\ A^0).

For vibrations which involve the motions of the atomic nuclei, the forces are roughly the same as for electrons, but the mass of the moving particles is larger by a factor of 1800 to 18,000. This means the frequency \( v = 1/2\pi (k/m)^{1/2} \) is smaller by a factor of \((1800)^{1/2}\) or so, corresponding to a wavelength of about 5\( \mu \). Since this wavelength lies in the infrared region (1\( \mu \) - 50\( \mu \)) we may expect to find vibrational transitions in the infrared spectrum. By infrared one studies primarily the vibrational motions of the molecules.

Vibrations of some simple molecules.

We will treat the vibrations of some simple molecules in some detail. In this way we will meet some general features which are equally applicable to the study of more complicated molecules.

a) The diatomic molecule\( \text{C} = \text{O} \) obviously can have only one vibration. The vibration, in a first approximation, can be described as an harmonic oscillator which corresponds to energy levels given by \( E_n = (n + \frac{1}{2})\hbar \nu_0 \). \( \nu_0 \) is the eigenfrequency of the vibration of the molecule.

\[ \begin{align*}
\text{At ordinary temperatures almost all molecules will be in the ground state, } E_0, \text{ where } n = 0, \text{ so that the only possible transitions are } 0 \rightarrow n \text{ transitions, corresponding to an absorption frequency } \nu = (E_n - E_0)/\hbar = n\nu_0. \text{ We may expect infrared absorption bands at } \nu_0, 2\nu_0, 3\nu_0, \text{ etc.} \\
\text{The principal absorption band at } \nu_0, \text{ usually called the fundamental, is much stronger than the overtones: } 2\nu_0 \text{ (first overtone), } 3\nu_0 \text{ (second overtone), etc. The absorption spectrum of } \text{CO} \text{ will look like} \\
\end{align*} \]

Fundamental for \( \text{CO} \): wave number= 2200 cm\(^{-1}\) or 4.54

b) \( \text{CO}_2 \) has more than one vibration. \( \nu_1 \) is the symmetric stretching vibration (stretching vibrations involve primarily a stretching of covalent bonds).
\[ v_1 \quad 0 \quad C \quad 0 \]

\[ v_2 \quad 0 \quad \leftarrow C \quad \rightarrow 0 \]

\[ v_3 \quad 0 \quad \uparrow \quad C \quad \downarrow 0 \]

Hence we would expect that CO₂ would give three strong absorption bands for the fundamentals. The spectrum, however, shows only two strong absorption bands. Apparently one transition just does not occur under the influence of light.

\[ 667 \text{ cm}^{-1} \quad 2349 \text{ cm}^{-1} \]

\[ 16\mu \quad 4\mu \]

To understand this we have to dig a little deeper into the mechanism of absorption. A vibration will absorb radiation only if there is an appreciable interaction with the light. The most prominent interaction is the interaction of the electric field of the light with charges which move during the vibration; that is, with a vibrating dipole of the molecule. Hence, a large vibrating dipole in the molecule will have a strong interaction with light and will consequently result in a strong absorption. If we examine the vibrations of CO₂, we see that \( v_3 \) is associated with a changing dipole. If the atoms bear charges, which they certainly do due to a difference in electronegativity between C and O, the bending molecule will have a dipole:

During the vibration this dipole continuously changes, and it will therefore interact with the light and cause absorption. The same is true of \( v_2 \):

\[ 0 \quad \leftrightarrow C \quad 0 \quad 0 \quad \leftrightarrow C \quad 0 \]

no dipole  dipole

However, vibration \( v_1 \) cannot be associated with a dipole, because of the symmetry of the motion:

\[ 0 \quad \leftrightarrow C \quad 0 \quad 0 \quad \leftrightarrow C \quad 0 \]

no dipole  no dipole

Therefore, this vibration will not give rise to any light absorption. Since the vibration will be "infrared inactive", the transition \( 0 \rightarrow v_1 \) is forbidden. This explains why we see only two infrared absorption bands due to \( v_2 \) and \( v_3 \).

In addition, we may easily guess which absorption band is due to \( v_2 \) and which to \( v_3 \). In \( v_2 \) the CO bond is stretched and requires more energy than the bending of the molecule occurring in \( v_3 \). Therefore, the force constant in \( v_2 \) will be larger, and the frequency will also be increased. Thus, the band at 16\( \mu \) is assigned to the deformation \( v_3 \); the band at 4\( \mu \) is assigned to the symmetric stretching vibration.

Now, what can the infrared spectrum teach us about CO₂? Suppose that CO₂ were not a linear molecule; then the symmetric stretching vibration \( v_1 \) would
be associated with a changing dipole. The fact that we find only two strong infrared absorption bands thus proves that CO₂ is a linear molecule.

We have seen that the intensity of the absorption depends on the varying dipole. This means that we can obtain the magnitude of this dipole from the intensity of the absorption band. For example, a measurement of the intensity of the ν₃ band gives us directly the bond moment of the C = O bond, a value which evidently cannot be obtained from dipole moment measurements, since the CO₂ dipole is zero.

The frequency of the vibration depends on the interatomic forces in the molecule. In the simple example of CO₂, a measurement of the absorption frequency gives directly the force constant of the CO bond, which is a measure of the bond strength.

**Rotation.**

In the gas phase, molecules can rotate freely thereby giving rise to a set of closely spaced energy levels:

\[
\begin{align*}
\text{n = 1} & \quad \text{rotation levels.} \\
\text{n = 0} & \\
\end{align*}
\]

This gives a fine structure of the vibrational spectrum. The vibrational transition actually consists of a great number of rotational - vibrational transitions. The CO vibration, for example, looks like:

\[
\begin{align*}
\text{The spacing of rotational lines is } 4 \text{cm}^{-1}.
\end{align*}
\]

From the spacing of the rotational lines one directly obtains the moment of inertia and, hence, the interatomic distance. For heavier molecules, the spacing between the rotational lines become smaller. If one works with a spectrometer of a moderate resolving power, one first observes a rather broad band, the envelope of the rotational fine structure.

In liquids, the rotational fine structure completely disappears since the molecules cannot rotate freely.

**Complicated molecules.**

In more complicated molecules, the number of independent vibrations is large (actually 3N - 6 for a molecule with N atoms). 3N = number of degrees of freedom, subtracting 3 for translations and 3 for rotation), and the spectrum will consist of many absorption bands:
Hence, infrared spectrum enables one to discover something about the structure of molecules. If an organic chemist has prepared a product but does not know what it is, (This may seem strange for people from industry since they usually know what they are making.), he prepares an infrared spectrum, and finds a band at 3600 cm\(^{-1}\) and one at 1700 cm\(^{-1}\). He can then correctly conclude that the molecule contains an O—H and a C=O group. With other information he may already have, this may be sufficient to identify the product molecule.

**Hydrogen bonding.**

Another instructive example of information which can be gained from infrared spectra relates to the phenomenon known as hydrogen bonding. We know that an O—H group tends to form hydrogen bonds with other oxygen atoms:

\[-\text{O—H} \cdots \text{O}\-\]

Since the O is slightly negative, and the H slightly positive the O—H will be stretched a little bit by the hydrogen bond. The O—H bond, then becomes a little weaker, and the force constant of the O—H vibration will diminish. Thus a hydrogen bonded O—H will have a lower stretching vibration. e.g. (1) A dilute solution of phenol in hexane exhibits no hydrogen bonding; the frequency is 3600 cm\(^{-1}\). (2) A solution of phenol in ethyl ether manifests hydrogen bonding; the O—H vibration frequency is 3362 cm\(^{-1}\).

Hydrogen bonding thus causes an appreciable frequency shift as phenol forms hydrogen bonds with the ether oxygen.

**Spectrum of pure compounds:** The band at 3300 cm\(^{-1}\) indicates hydrogen bonding in dilute solutions of catechol (Dihydroxy benzene) in hexane. This leads to the conclusion that this compound has internal hydrogen bonding, possible only for the ortho configuration. From an infrared spectrum of a mixture of ortho and para, we can easily determine the amount of ortho.

Summarizing, we may say that the infrared spectrum can give us fundamental molecular properties such as force constants, charge distribution, etc. It can be a useful tool in structure determination and in analytic procedures.
TERMOLECULAR REACTIONS

Kevin P. Murphy, '55

According to current theory, nucleophilic displacement reactions occurring at a saturated carbon atom may take place by one of two mechanisms or a combination of both.

The first, the ionization mechanism, is designated as an S\textsubscript{N}1 reaction, i.e., substitution nucleophilic 1st order. The driving force in the S\textsubscript{N}1 mechanism is thought to be a pull or frontal attack on a substituent by the solvent or some electrophilic solute which forms hydrogen bonds with, or otherwise solvates, the leaving atom or group. This bonding causes a weakening of the original carbon substituent bond and allows the molecule to ionize in the rate determining step. The kinetics of the reaction are first order when an excess solvent is used. An example of the above is the solvolysis of triphenylmethylbromide in methanol. The C-Br bond is weakened by solvolysis of the Br by methanol; the compound ionizes, and the methoxy group enters. In studying the kinetics of the S\textsubscript{N}1 type reaction, most investigators used large excesses of hydroxylic solvents. They were, therefore, unable to determine the kinetics order with respect to the solvent.

C. G. Swain, by using an inert solvent, has been able to determine the kin-}

(\textit{1}) Edited from a term paper submitted December, 1955.

etic order with respect to all nucleophilic and electrophilic species present. The results of his experiments indicate that the rate determining ionization step occurs by a termmolecular rather than monomolecular mechanism. The ionization is a result of concomitant or "concerted" solvating attacks on both the carbon and the halogen.

In his work Swain reacted triphenylmethylichloride with methanol to give the triphenylmethyl ether.

\[(\text{C}_6\text{H}_5)_3\text{CCl} + \text{HOCH}_3 \rightarrow (\text{C}_6\text{H}_5)_3\text{COCH}_3 + \text{HCl}\]

A tertiary amine was used to take up the hydrogen halide and render the reaction irreversible. The kinetics of the triphenylmethyl chloride and methanol reaction were found to be exactly third order, first order in triphenylmethyl chloride and second order in methanol. The exact third order kinetics indicates that some type of pure mechanism is involved.

Swain next substituted phenol for methanol. The phenyl ether was formed but at about one fiftieth the rate of the other. This reaction likewise followed third order kinetics. If the reaction of triphenylmethylichloride and phenol proceeded by an ordinary S\textsubscript{N}1 mechanism it would be expected that the rate would increase over that of the triphenylmethylichloride and methanol since phenol forms a stronger bond with halogens than methanol and would cause the ionization to take place more rapidly. The slower action of the phenol can be explained by assuming that solvation of the carbon is
necessary, and phenol, because of its bulk, would be less effective in this solvation than methanol.

When the reaction was run with both methanol and phenol present only methanol was consumed as long as it was present. The rate of the reaction in the presence of phenol was found to be seven times faster than that using methanol alone. The best explanation for this increase in the rate in the presence of phenol seems to be that the solvation of both the halogen and the carbon are required in the reaction. Phenol is an excellent solvating agent for halogens but poor for solvating carbon. Since solvation of both is required by this explanation, phenol alone reacts slowly. Methanol is a moderate solvating agent for halogens and an excellent one for carbon, hence alone it reacts at a moderate rate. When both are present each performs the function to which it is best suited and a very high rate results. This reasoning can be summarized by the following.

\[(C_6H_5)_2CCl + CH_3OH \rightarrow \text{moderate rate.}\]

The methanol is solvating both the carbon and the halogen.

\[(C_6H_5)_2CCl + C_6H_5OH \rightarrow \text{very slow.}\]

Phenol is solvating both carbon and halogen.

\[(C_6H_5)_2CCl + CH_3OH + C_6H_5OH \rightarrow \text{very fast.}\]

The methanol solvates the carbon and the phenol solvates the halogen.

The kinetic evidence indicates that a simultaneous attack on both the carbon and the halogen is necessary to effect the reaction. The rate determining step is therefore a "concerted" termolecular push-pull solvation and is a two step process involving a solvated ionic carbonium salt intermediate. Swain has given this mechanism the name "carbonium ion mechanism."

The second mechanism which is possible in nucleophilic displacement is the SN2. The rate determining step in this type of reaction is thought to consist of a "push" or nucleophilic attack from the rear by the entering atom or group which has an unshared pair of electrons. An example of this type of reaction is that of methyl bromide and pyridine in benzene.

\[
\begin{align*}
\text{H} & \quad \text{N}^- \quad \text{C} \quad \text{Br}^- \\
& \quad \text{H} \quad \text{H} \\
\end{align*}
\]

This is a one step process, which Swain has given the name "direct mechanism." This reaction proceeds at a moderate rate in benzene solution. The reaction is second order. The addition of mercuric bromide increases the rate 12% methanol 13%, phenol 42%, and p-nitrophenol 64%. This increase in the rate can be explained by assuming that the addition of mercuric bromide, methanol, or phenol solvates the bromine atom of methyl bromide in front while pyridine simultaneously attacks the carbon from the back.
This is a termolecular reaction of the unsaturated compound, the halide ion, and the halogen molecule. This mechanism explains the effect of the halide ion on the reaction since it takes part in the rate determining step.

Various other reactions reported appear to be termolecular in nature. The alkaline hydrolysis of silanes, the cleavage of ethers with hydrogen bromide, the mutarotation of glucose, and the hydrogen chloride catalyzed addition of hydrogen to olefins exhibit third order kinetics and are probably termolecular.

References:
FELLOWSHIP WINNER

GEORGE P. FLYNN

Once again, a Providence College student has been honored with a National Science Foundation Fellowship, the recipient this year being George P. Flynn.

Fellowships are awarded on the basis of a student's score on the Graduate Record Examination, letters of recommendation from professors associated with him, and his academic record. An award carries a stipend of $1600 plus fees and tuition to be used by the recipient at any university of his choice.

Mr. Flynn, a native of Warren and a graduate of Warren High School, will continue his studies in physical chemistry at Brown University. George, who will graduate in June as the "top" man in the senior class, has never failed to place high on the Dean's Honor List and has compiled a perfect "A" average while doing so.

Other Providence College men who received honorable mention for this award are: John Graham, chemistry; Anthony Fratiello, chemistry; and Robert Gould, physics.

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DAPFYNITIONS

Below are some definitions brewed in a hilarious moment by science students at the Abraham Lincoln High School. These were subsequently printed in the school paper, Lion Tales.

CHLORINE. A dancer in a night club.

COPPER. A man who gives admission slips to traffic courts.

CARBON. Storage place for street cars.

BARIUM. What you do with dead people.

CATALYST. A western ranch owner.

BORON. What most school classes are.

ATOM. Eve's husband.

TENSION. An Army order.
In recent years there has been a great increase in research in the field of high pressures. This term is usually applied to pressures of the order of thousands of atmospheres. This field is now of special interest in conjunction with high temperature research, the two often being associated.

The importance of this subject is shown by the fact that over 99% of the matter in the universe exists under pressures greater than 1000 atmospheres. For example, the pressure at the ocean bottom is 1000 atm, that at the center of the earth about \(5 \times 10^6\) atm, and that at the center of the sun of the order of \(2 \times 10^{11}\) atm. In comparison, the initial pressure in an atomic bomb explosion is greater than \(10^{11}\) atm. The pressures now experimentally attainable (\(>10^8\) atm) are sufficiently high to justify the statement that geology is now an experimental science.

Nearly all the fundamental work in this field has been done by P. W. Bridgman of Harvard University, who has developed the principal techniques and apparatus since 1905. Prior to 1905, the maximum pressure attainable was 3000 atm. Bridgman then invented a means of preventing leakage, thereby reaching 20,000 atm. The next improvement was a method of pushing the pressure vessel into a conical support device, so that the support increased with applied pressure, giving a maximum of 50,000 atm. To attain higher pressures, it was necessary to use two stages of support, one within the other, with a transmitting fluid between. With this liquid under 30,000 atm, it is possible to reach 100,000-110,000 atm, in the inner vessel (only 1.8 mm. long). An additional aid was the development of Carboloy for the pressure vessels, a sintered tungsten carbide containing cobalt, the strength of which increases under pressure. Still higher pressures, up to 400,000 atm, have been attained by applying large stresses to small areas, but only qualitative effects can be thus studied.

The most accurate device for measuring high pressures is the free piston gauge, which measures the actual thrust on the piston. Since this is unwieldy and inconvenient, it is used only for the calibration of secondary instruments. The most common method is the measurement of the change in the electrical resistance of manganin under pressure.

Among the properties easiest to study are volume changes in solids and liquids, including phase changes. In particular, it has been found that the melting-point curve for nearly all subs-

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(1) Edited from a seminar given October 17, 1956.
stances rises indefinitely with increased pressure, showing no critical point, and following the empirical equation:

\[ p + a = C \cdot T^b \]

which agrees with theory.

The compressibility of several elements is shown in Figure 1. The sharp breaks in several curves in this figure indicate phase transitions between polymorphic forms. This can be determined by analysis of the crystal structure with X-rays while under pressure, or by removing the pressure at extremely low temperatures (slowing the reverse transitions). Polymorphic forms have been found to be far more common at high pressures than under ordinary conditions. In the most extreme case, d-camphor, eleven solid forms are known below 35,000 atm.

There are four anomalous substances (water, bismuth, antimony, and gallium) whose ordinary solid forms have a greater volume than the liquid, resulting from their abnormal loose crystal structures. Therefore, following the Clausius-Clapeyron equation, the melting point decreases with increasing pressure until a point is reached at which the loose structure collapses. This occurs for water at -22°C and 2200 atm, above which the melting point increases normally. There are six stable forms of ice, and the other three substances show exactly analogous phase diagrams.

Although all the phase changes discussed above are reversible, several irreversible changes have been discovered. The first of these was the change of white phosphorus to a black form at 12,000 atm. and 200°C, or at 30,000 atm. and room temperature. Red phosphorus changes similarly at 50,000 atm. Another example is the transformation of CS₂ to a dense black solid at 175°C and 40,000 atm.

However, the most important irreversible change achieved is the often
attempted synthesis of diamonds from graphite. It had been found that this could not be done by pressure alone, but required high temperature in addition. In 1954, General Electric developed a press which could sustain conditions of 3000°K and 60,000 atm. for several hours. Using this apparatus, it was found possible to form small diamonds, the largest only 1/16 inch long, but identical with natural diamonds.

In regard to purely chemical effects, the rates of reactions are considerably increased by high pressures, and the position of equilibrium is shifted according to Le Chatelier’s Principle. These effects apply principally to gas reactions at relatively low pressures, and are of mainly industrial interest.

The phase diagrams of alloys and solutions have also been determined by measuring resistance or conductivity. The effects of high pressures on many other physical properties have been extensively studied. The most pronounced effect found is that on viscosity, which is often increased by a factor of 10³. Other properties studied include mechanical properties (elasticity, ductility, tensile strength, etc.), specific heats, thermal conductivity, and electrical resistances. The mechanical properties mentioned increase under pressure, thus strengthening the apparatus itself.

In order to formulate a theory of high pressure phenomena, it is necessary to consider the actual effects of pressure. At low pressures, the behavior of gases follows the kinetic theory. Liquids are formed when the molecules are forced into effective contact, and the spaces between the molecules are then squeezed out. In the solid state, the molecules and atoms themselves are deformed. It may be expected that at still higher pressures the electronic structures of the atoms would begin to collapse. This has actually been observed in two cases. Cesium shows a 17% decrease in volume at 45,000 atm., which has been theoretically explained as a shift of the outermost electron from a 6s to a 5d orbital. A similar transition occurs in cerium. Further, it may be noted here that barely measurable changes in the decay rate of radioactive nuclei have been produced by pressures of 100,000 atm.

By extrapolation of these phenomena, theoretical predictions have been made of the effects of very high pressures, greater than 10⁶ atm. At pressures above 10⁷ atm., matter breaks down to an "electron gas" (Fermi gas), in which all the electronic shells have collapsed as such, and which follows the law:

\[ pV = R^*T \]

In this state, which exists in the interiors of stars, the rigidity of the
solid disappears, the compressibility resembling that of a gas. Finally, in the extreme limit (at about $10^{23}$ atm.), the nuclei themselves are squeezed into contact. This "nuclear state" is highly unstable and results in supernova explosions of dense stars.

References:

2. Bridgman, P. W., Rev. Mod. Phys. 18 1 (1946)
3. Bridgman, P. W., Endeavour, 10, 63 (1951)

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1 EPOXIDES

Pasco R. Santurri, '57

An epoxy or oxirane compound is defined as one which contains a three membered carbon-carbon-oxygen ring. For example,

\[
\begin{align*}
\text{CH}_3 - \text{CH}_2 \\
\end{align*}
\]

is epoxyethane and

\[
\begin{align*}
\text{CH}_3\text{CH}=\text{CH}_3
\end{align*}
\]

is 1,2-epoxypropane.

Broadly speaking, we may define epoxidation as the reaction of an unsaturated compound with an oxidizing agent to give the epoxy compound.

The reaction of an organic peracid with an olefinic material leads to an epoxy or oxirane compound:

\[
\begin{align*}
\text{RCO}_2\text{H} + \cdot\text{C} = \text{C} - & \rightarrow \\
\text{RCO}_2\text{H} + \text{CO}_2\text{H}
\end{align*}
\]

olefin + peracid \rightarrow epoxide + organic acid

Depending upon conditions, this reaction may proceed further with cleavage of the epoxide ring to yield hydroxy-acyloxy derivatives or glycols.

(1) Edited from a Seminar given April 30, 1956.
acetates instead of epoxides. The first successful epoxidation with peracetic acid was reported by Smith and Gaster who obtained methyl 9,10,12,13-diepoxystea-
rate.

\[
\text{CH}_3\text{(CH}_2)_4\text{CH-CH-CH}_2\text{-CH-CH(CH}_2)_7\text{COOCH}_3
\]

However, the yield was very poor. In a systematic study of the reaction of unsaturated compounds with peracetic acid in an acetic acid solution and in inert solvents, it was found that epoxides were obtained when an inert solvent was used. The yields in such cases were very good. They concluded that the behavior of peracetic acid on olefins was the same as perbenzoic acid on olefins. However, the oxirane or epoxy ring is opened when peracetic acid is in an acetic acid solution since the epoxy ring further reacts with acetic acid. Findley, Swern, and Scanlon, found that good yields of epoxy compounds could be obtained if the temperature of the reaction was held between 20° - 75° C. Also, the reaction time should be as short as possible in order to prevent the opening of the ring.

Performic acid is also used as an epoxidation reagent. Usually 0.25 to 0.50 moles of formic acid per mole of unsaturation and one mole of \( \text{H}_2\text{O}_2 \) per double bond are used for good yields of epoxides.

Epoxycethane, or ethylene oxide as it is more commonly known, can be prepared by the air oxidation of ethylene.

\[
2\text{CH}_2=\text{CH}_2 + \text{O}_3 \rightarrow 2\text{CH}_2=\text{CH}_2\text{O}
\]
Epoxyethane may also be prepared by reacting ethylene chlorohydrin with calcium hydroxide:

\[ 2\text{HO-CH}_2-\text{CH}_2-\text{Cl} + \text{Ca(OH)}_2 \rightarrow 2\text{CH}_2-\text{CH}_2+\text{CaCl}_2 + 2\text{H}_2\text{O} \]

Ease of epoxidation depends considerably upon the nature of the unsaturated substance. Epoxidation of isolated double bonds, such as are present in most fatty acids and oils, occurs easily in 2 to 4 hours as compared with 28 hours under the same conditions for terminally unsaturated compounds such as 1-octadecene. A study of the reaction rates of peracids on olefins showed that substitution of alkyl groups for the hydrogen atoms attached to the double bond increased the rate. However, the rate was decreased when such electron attracting groups such as carbonyl or carboxyl groups were attached to, or in close proximity to, the double bond.

Unsaturated compounds are the raw material for epoxidation reactions. Oils and fats of animal, vegetable and marine origin are a main source of unsaturated fatty acids. These may contain 1,2, or 3 double bonds per chain. Epoxy plasticizers are based on this type of raw material. Unsaturated hydrocarbons obtained in petroleum cracking and refining provide a cheap source for epoxidation.

Due to the strained configuration of the epoxy ring, epoxides are quite reactive. Listed below are a number of reactions showing the activity of the epoxy compound.

\[
\begin{align*}
\text{C-O-} + \text{H}_2\text{O} & \rightarrow \text{C-OH} \quad \text{(1)} \\
\text{C-O-} + \text{HCl} & \rightarrow \text{C-C-} \quad \text{OH Cl} \quad \text{(2)} \\
\text{C-O-} + \text{RCO}_2\text{H} & \rightarrow \text{C-C-} \quad \text{OH OCOR} \quad \text{(3)} \\
\text{C-O-} + \text{NH}_3 & \rightarrow \text{C-C-} \quad \text{OH NH}_2 \quad \text{(4)} \\
\text{C-O-} + \text{HCN} & \rightarrow \text{C-C-} \quad \text{OH CN} \quad \text{(5)} \\
\text{C-O-} + \text{H}_2\text{S} & \rightarrow \text{C-O-} \quad \text{OH SH} \quad \text{(6)} \\
\text{C-O-} + \text{C}_6\text{H}_6 & \rightarrow \text{C-C-} \quad \text{OH C}_6\text{H}_6 \quad \text{(7)} \\
\text{C-O-} + \text{ROH} & \rightarrow \text{C-C-} \quad \text{OH OR} \quad \text{(8)} \\
\text{C-O-} + \text{R}_2\text{NH} & \rightarrow \text{C-O-} \quad \text{OH NR}_2 \quad \text{(9)} \\
\text{C-O-} + \text{RMgX} & \rightarrow \text{C-C-} \quad \text{OH R} \quad \text{(10)}
\end{align*}
\]

The use of synthetic resins as coating materials, in the late twenties, was brought about by the improvements in durability, resistance, hardness and adhesion of these resins. Most of the coating materials developed prior to 1941 had a common characteristic -- an ester linkage in the molecule. Though this chemical characteristic was partly responsible for the fact that such materi-
als were used for coatings, it was the point in the molecule which was constantly attacked.

In early 1939 three men working under Dabney decided to organize a systematic search for a coating material which did not have this ester linkage. At that time the problem had some of the aspects of looking for "dry water". However in 1941, Long, Scott, and Greenlee outlined types of molecules which might hold possibilities. Their work led them to compound a resin from epichlorohydrin and bisphenol A:

\[
\text{HO-} \text{CH}_{2}\text{-CH-CH}_{2}\text{OH} + \text{CH}_{2}\text{-CH-CH}_{2}\text{Cl} \xrightarrow{\text{Ag} \; 75^\circ \text{C}} \text{NaOH} \\
\text{CH}_{3}\text{-CH-CH}_{2}\text{-}\text{O}\text{-CH}_{2}\text{-CH-CH}_{2}\text{OH} \xrightarrow{\text{NaCl + H}_2\text{O}} \text{CH}_{3}\text{-CH-CH}_{2}\text{-CH}_{2}\text{O}\text{-CH}_{2}\text{-CH-CH}_{2}\text{Cl}
\]

The commercial resins are mixtures of polymers, with \( n \) varying from 0 to 10, indicating molecular weights from approximately 400 to 8,000.

These resins owe their versatility to the following properties:

1. Wetting of and adhesion to a wide variety of surfaces.
2. Curing without the evolution of by-products.
4. Resistance to many acids and most alkalies.
5. High mechanical strength.
6. Good thermal stability.
7. Exceptional water resistance.

The production of epoxy resins has been recently estimated to be about seventy-five million pounds per year.

Epoxy adhesives are now widely accepted in the aircraft industry. Tests underway indicate that before long we may be flying in aircraft glued with epoxy resins. This type of resin has shown itself to be ideal for tooling applications and dies. Storage tanks for crude oil are also being made of epoxy resins. Children's toys are made of this polymer.

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