Thermal Stability as a Function of Chemical Structure

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IN THIS JET and space age more and more emphasis is on thermal stability. For lubricants and hydraulic fluids it is apparent that other properties such as viscosity, pour point, oxidative stability, and vapor pressure are important, but such properties are more amenable to improvement by additives and minor structural modifications than is thermal stability. There is no systematic recording in the chemical literature of the thermal stability of organic compounds under the same conditions. Many of the chemical literature data on thermal stability are based on the stability of a material passing through a hot tube and on observations made upon distillation.

This paper reports on a comparison under the same conditions of the thermal stabilities of over 100 organic compounds in 12 chemical classes and the relation of these data to structure. The test method and a large portion of the data reported here resulted from a search for materials with a minimum thermal stability of 700° F. (*5*).

MEASUREMENT OF THERMAL DECOMPOSITION TEMPERATURES

Theory. A practical thermal stability screening test applicable to a wide range of compounds must be based on some readily measurable property change common to all thermal decompositions and as directly related to the true rate of decomposition as possible. The most general change in properties in the thermal decomposition of organic molecules is an increase in the vapor pressure of the system brought about by cleavage of the molecule into smaller, more volatile fragments. This physical change has the advantage over others such as weight loss, viscosity change, and heat of reaction, of being related to the true rate of thermal decomposition by a simple although usually unknown proportionality constant.

A close relation between the isothermal rates of pressure rise and decomposition rates can be readily shown. If a compound B decomposes into j molecules of decomposition products,

$$\mathrm{B} \rightarrow D_1 + D_2 + \text{---} D_j \tag{1}$$

then the rate of disappearance of B, dn_B/dt, is given by

$$\frac{dn_B}{dt} = -kn_B^{\nu} \tag{2}$$

where k is the rate constant, n_B is the concentration of B, and ν is the order of the reaction. The rate constant, k, varies with temperature according to the Arrhenius rate law,

$$k = Ae^{-E/RT} \tag{3}$$

where A is a frequency factor and E the activation energy. If each molecule of B decomposes to introduce b molecules of decomposition products into the vapor phase at a rate dn_D/dt then, assuming ideal gas behavior, the relation between the rate of pressure rise, dp/dt, and dn_B/dt is

$$-b\,\frac{dn_B}{dt} = \frac{V_g\,dn_D}{V_B\,dt} = \frac{V_g}{V_B RT}\,\frac{dp}{dt} \tag{4}$$

where V_g is the volume of the gas phase and V_B the volume of the liquid phase. For a given decomposition, therefore, dp/dt will be related to dn_B/dt by the simple factor b adjusted for temperature and the relative volume of the gas and liquid phases. Since determination of b requires detailed information about the reaction, the authors have assumed, for the purposes of a thermal stability test, that it is the same for all compounds.

For all compounds reported in this paper a plot of log dp/dt *vs.* $1/T$ was a straight line which showed that, as expected, dp/dt follows an Arrhenius rate law analogous to Equation 3.

$$dp/dt = A'e^{-E'/RT} \tag{5}$$

This relationship has allowed the authors to summarize the experimental data by reporting constants A' and E' and to interpolate from the data a decomposition point, T_D, for the purpose of comparing the thermal stabilities of different compounds. The decomposition point is defined as the temperature $T_D°$ F. at which dp/dt = 0.014 mm. Hg per second or 500 mm. Hg per 10 hours.

The theoretical relation between E and E' can be readily shown as follows. Solving Equation 5 for E' with data obtained at temperature T_1 and T_2 gives

$$E' = -\frac{RT_1T_2}{T_1 - T_2}\ln\left[\left(\frac{dp}{dt}\right)_2 \bigg/ \left(\frac{dp}{dt}\right)_1\right] \tag{6}$$

and solving Equations 3 and 4 for E gives

$$E = -\frac{RT_1T_2}{T_1 - T_2}\left\{\ln\left[\left(\frac{dp}{\mathrm{dt}}\right)_2 \bigg/ \left(\frac{dp}{dt}\right)_1\right] + \ln\frac{T_1}{T_2}\right\} \tag{7}$$

Subtracting Equation 6 from Equation 7 gives

$$E = E' - \frac{RT_1T_2}{T_1 - T_2}\ln\frac{T_1}{T_2} \tag{8}$$

and applying L'Hospital's rule to obtain the limiting value of the temperature term in Equation 8 gives

$$E = E' - RT_m \tag{9}$$

where T_m is the mean temperature for the range of observations. The difference $E - E'$ will thus amount to about 2% for observations near 800° F. and is independent of b.

The relation between A and A', derived from Equations 3, 4, 5, and 9, is

$$A = \frac{V_g}{V_B n_B^{\nu} bRTe}\,A' \tag{10}$$

In general, $A \approx 10^{-6}A'$. Substituting the following data for *m*-bis(*m*-phenoxyphenoxy)benzene in Equation 10, $V_B = V_g$, $\nu = 1$, $b = 1$, $e = 2.714$, $n_B = \frac{1\text{ cc.} \times 1\text{ gram/cc.}}{446.5\text{ gram mole}^{-1}}$, $T = 456°$ C., $R = 760 \times 82.06$ mm. Hg cc. per mole per degree, yields $A = 3.6 \times 10^{-6}A'$ per second.

The decomposition point was chosen as the basis for comparing thermal stabilities of organic compounds because it affords a convenient single number for comparing the stability of different compounds, a number which is easier to visualize (and to determine) than the combination of values E' and A' which define the rate constant. Use of the rate constant, k, for this screening test comparison is less practical than T_D because, as shown by Equation 11,

$$k = -\frac{1}{n_B^{\nu}}\frac{dn_B}{dt} = \frac{V_g}{bn_B^{\nu}V_BRT}\frac{dp}{dt} \tag{11}$$

the evaluation of k involves knowledge of the quantity ν as well as of b.

The decomposition points of a series of compounds are the temperatures at which all have the same isothermal rates of pressure rise. Except for certain factors which could be determined, but which in the present study are usually unknown, decomposition points could give precise comparisons of thermal stabilities analogous to the use of boiling points for comparing volatility. Unknown or undetermined factors which limit the validity of comparisons of stability by the test method described herein include factors b, n_B, and V_g/V_B. Knowledge of these factors would enable one to calculate the fractional rate of decomposition $(1/n_B)\ dn_B/dt$ from measured values of dp/dt using Equation 4; however, neglect of these factors does not lead to serious errors in general, as is shown in the following discussion.

The effect of the number of decomposition fragments b is shown in Table I. Each time the number of fragments is doubled, the decomposition point equivalent to one volatile fragment per decomposing molecule increases by about 18° F. It seems likely, however, that a single reaction or reaction series accounts mainly for decomposition products from a given compound and that there are only one or two volatile decomposition products, so that the assumption that b is unity should seldom introduce in the decomposition point an error larger than 18° F.

The effect of neglecting n_B on the comparison of stabilities is to cause compounds of larger molar volume to appear more stable. Thus, if two compounds have equal decomposition points by this test, the compound with the larger molar volume must decompose at a fractional rate higher than the other. For a difference of 10% in molar volume the fractional rate would be about 10% higher, or stated another way, at a 2° to 3° F. lower temperature, its fractional rate of decomposition would equal that of the compound with the lower molar volume.

Differences in thermal expansion may cause the volume available to gaseous decomposition products to vary up to 10% for different samples. A resulting 10% difference in apparent rate corresponds to only a 2° F. difference in decomposition point. In compounds having widely separated (80° to 270° F.) decomposition points this difference amounts to ca. 6° F.

This discussion has pointed out the variables which are neglected in comparing the thermal stability of compounds by their decomposition points. The evaluation of the magnitude of the possible error thus incurred shows that differences in decomposition points of two compounds greater than 18° F. generally indicate significant differences in their thermal stability.

Table I. Effect of Number of Fragments on Decomposition Point

Sample No.	13	1	42
Compound	Bis(2-ethyl-hexyl) Sebacate	Octacosane	*m*-Bis(*m*-phenoxy-phenoxy)-benzene
No. of fragments[a]	Temperature, ° C.		
$b =$ 0.5	264	341	443
1	274[b]	350[b]	453[b]
2	283	360	465
4	293	369	477
A', mm. Hg/sec.	1.5×10^{16}	2×10^{18}	2×10^{17}
E', kcal.	45.1	57.6	63.8

[a] Number of fragments, b, is the number of gaseous molecules formed per molecule thermally decomposed.

[b] Temperatures in this row are decomposition points determined by the method described. Other temperatures were determined graphically by translating the experimental curves by amounts 2, 0.5, and 0.25 times the observed rates of pressure rise.

Measurement of Thermal Stability. Isothermal rates of pressure rise due to the thermal decomposition of a compound are measured in a modification of Smith and Menzies' static isoteniscope (*3, 14*) originally designed for vapor pressure determinations.

APPARATUS. A schematic diagram of the thermal stability apparatus consisting of isoteniscope, constant temperature bath, and vacuum-gas handling system is shown in Figure 1.

The modified isoteniscope (Figure 2) consists of a manometric U-tube joined by one arm to a sample bulb and by the other to an external system for measuring pressure. The spherical sample bulb of Smith and Menzies' isoteniscope has been changed to a horizontal cylinder of ca. 4.7-ml. volume. By this change, the vapor to liquid volume ratio can be reduced from 4 to 1 in order to magnify the effect of the gaseous decomposition products on vapor pressure without decreasing the samples' surface to volume ratio of about 2.5. A large surface area and small depth of sample fluid facilitate equilibration of decomposition products between the vapor and liquid phases. A receiver arm is provided on the upper stem of the isoteniscope to collect liquid decomposition products which sometimes accumulate

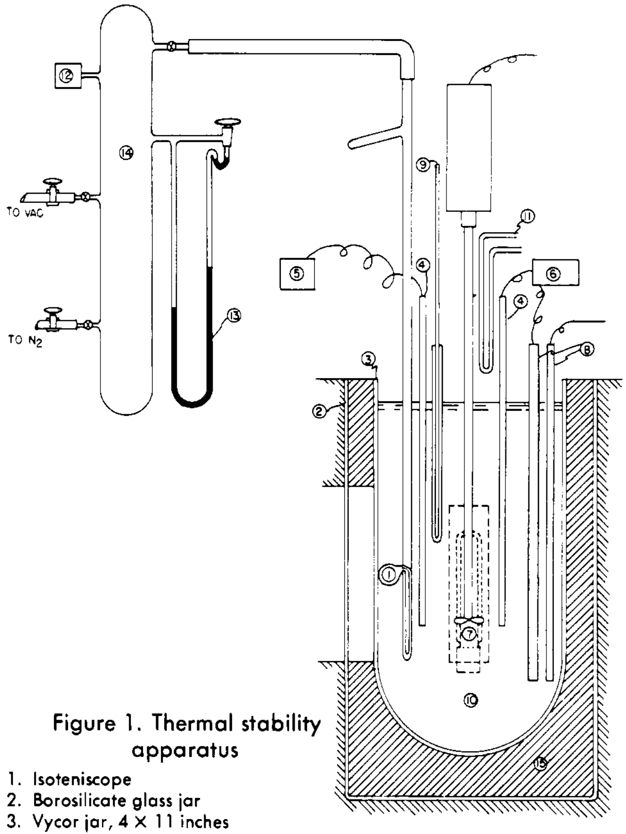


Figure 1. Thermal stability apparatus

1. Isoteniscope
2. Borosilicate glass jar
3. Vycor jar, 4 × 11 inches
4. Stainless steel resistance thermometer (Leeds & Northrup No. 8911-L-12)
5. Wheatstone bridge (Leeds & Northrup No. 8062)
6. Temperature controller (Hallikainen Thermotrol Model 1053)
7. Showcase bulb, 60-watt
8. Firerod immersion heater, 770-watt (Watloro Electric Mfg. Co. No. J 12JX2A)
9. Mercury thermometer 100°–600° C. in stainless steel well
10. Bath fluid. 54.5% KNO_3, 27.3% $LiNO_3$, 18.2% $NaNO_3$ (*6*)
11. Copper cooling coil
12. Thermocouple vacuum gage (Consolidated Electrodynamics Corp. type GTC-100)
13. Mercury manometer
14. Expansion chamber, 1 liter in volume
15. Glass fiber insulation

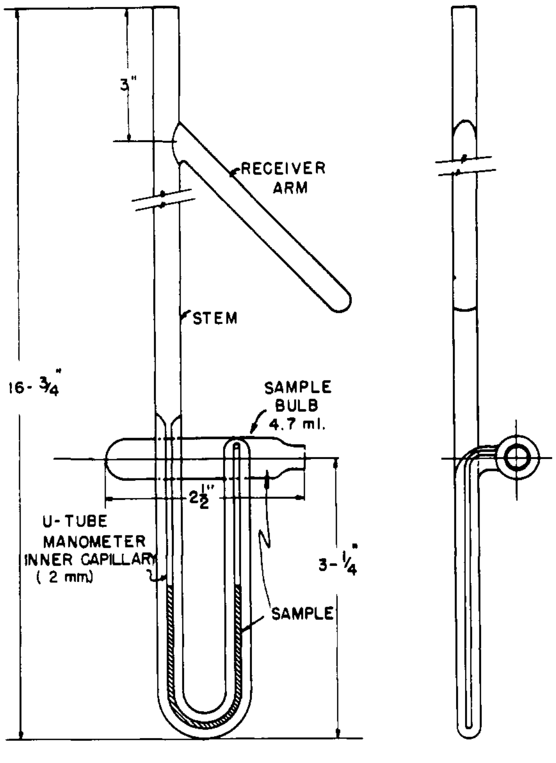


Figure 2. Isoteniscope

and can be removed by distillation. The material to be tested is used to form a differential manometer in the U-tube, for detection of equilibrium between the vapor pressure of the material in the sample bulb and the external measurable pressure. The isoteniscope (Figure 2) is inexpensive and is discarded after one use.

The constant temperature bath (Figure 1) is designed to be adjusted quickly to any selected temperature between 150° and 500° C. and can be controlled within ±0.02° C. This close control is necessary to minimize variations in the vapor pressure of the sample during measurement of very small isothermal rates of pressure rise at the lower end of the measurable range. For such versatility and precision, a liquid rather than a metal block, air or vapor bath was essential, and an eutectic mixture of nitrates (*4*), f.p. 120° C. (10, Figure 1) was chosen as bath fluid. Heat and control are provided by a variable 770-watt continuous heater (8, Figure 1) and a 770-watt intermittent heater (4, 6, and 8, Figure 1) operating through a resistance bridge laboratory temperature controller using proportional control with reset. The bath temperature can be lowered quickly by insertion of a coil of copper tubing (11, Figure 1) circulating tap water. When the bath temperature is controlled it is measured within ±0.1° C. by means of a stainless steel-jacketed platinum resistance thermometer (4 and 5, Figure 1) calibrated against a National Bureau of Standards platinum resistance thermometer. When the temperature is changed, it can be observed quickly with a 100° to 600° C. mercury in glass thermometer (9, Figure 1).

PROCEDURE. The sample bulb of the isoteniscope is half-filled with sample and sealed. The isoteniscope is then attached to the vacuum-gas handling system, evacuated, checked for leaks both with a Tesla coil and the thermocouple gage (12, Figure 1), and carefully outgassed by heating with a gas flame. During the outgassing, the sample is refluxed vigorously up into the stem of the isoteniscope.

The isoteniscope is next placed in the bath which is at 200° C., and the sample is forced back into the sample bulb with high-purity nitrogen. The pressure is then reduced to 1 mm. of Hg, and the bath temperature is raised at a rate of about 4° C. per minute. When the sample begins to boil, enough is allowed to distill to half-fill the manometric U-tube, and, as the temperature continues to rise, the U-tube is kept in balance by carefully admitting nitrogen to the gas system. The pressure (±0.2 mm. of Hg) on the mercury manometer and temperatures (±0.3° C.) on the glass thermometer are observed periodically to obtain vapor pressure data. These data are plotted (log *p* *vs.* $1/T°$ K) during the run, so that decomposition can be detected by the departure of the vapor pressure data from a straight line.

Bath temperature is then controlled at the highest temperature at which a rate of pressure rise can be readily measured, usually at about 0.5 mm. of Hg per second at this first point, and measurements are made until successive determinations give a constant value for dp/dt. Rates are then measured at two or preferably three or four successively lower temperatures at intervals of 15° to 25° C. These isothermal rates are plotted as log dp/dt *vs.* $1/T$ ° K on the same graph paper used for vapor pressure. Better reproducibility of rates is obtained by starting at the high temperature end of the measurable range, because any volatile or unstable impurities are largely eliminated at higher temperatures and their effects are minimized before lower rates are measured.

When the pressure in the sample bulb reaches 1 atm. because of the accumulation of volatile decomposition products, the nitrogen pressure is reduced to allow the decomposition products to distill through the U-tube until the pressure approaches the equilibrium vapor pressure of the sample. Then the U-tube manometer is balanced and rate measurements are resumed.

TREATMENT OF DATA. The primary data—the isothermal rates of pressure rise—are plotted on graph paper having as ordinate three logarithmic cycles and as abscissa degrees centigrade to scale of reciprocal absolute temperature. The best straight line is drawn through the points of log (dp/dt) *vs.* $1/T$. The decomposition point, T_D ° F., is interpolated directly from this plot as the temperature where dp/dt = 0.014 mm. of Hg per second. The activation energy, E', which can be calculated from Equation 6 is, in practice, determined graphically from the slope of the Arrhenius plot using a graph of E' *vs.* angular slope. The frequency factor, A', can be calculated by Equation 12 from E' and T_D:

$$\log A' = \log (0.014) + E'/2.303\,RT_D\,°\mathrm{K}. \qquad (12)$$

In practice it is determined graphically from isotherms of log A' *vs.* E' for various temperatures T_D from 350° to 1000° F.

Time required for this test, including processing of the data, is 8 hours.

The "useful life" of a compound (Table II) at a given temperature can be estimated from Equation 13 using constants obtained in this test.

Reproducibility of decomposition points T_D by this test is ±4° F., while it is estimated that errors in E' are ±2 kcal. per mole and in log A' they are ±1. Stability data reported herein are believed to stand within these limits, unless indicated as approximate. Approximate results are those based on data which were excessively scattered, or insufficient to establish a straight-line Arrhenius plot. One cause of this is presumed to be the presence of minor amounts of volatile or unstable impurities which were not completely eliminated by measuring the rates at points in a descending order with temperature. Other causes of scatter might be multiple mechanisms, catalytic impurities, or changes in distribution of decomposition products between liquid and gas phases as a result of changes in pressure, temperature, or quantity of decomposition products.

THERMAL STABILITY OF ORGANIC COMPOUNDS

In the following sections are data from thermal stability measurements of over 100 organic compounds representing

12 chemical classes. The authors have attempted to correlate these data with molecular structure on the basis of current concepts of bond strength, resonance, nature of the chemical bond, reaction mechanisms, and free radicals. These correlations are, of course, speculative, since they are based on screening data and are intended to serve as a guide in designing more thermally stable molecules rather than as a definitive description of thermal decomposition of organic compounds.

Hydrocarbons. Representative aliphatic and aromatic hydrocarbons and several closely related compounds are listed in Table III.

The thermal stability (T_D = 662° F.) of octacosane (compound 1), a straight-chain paraffinic hydrocarbon, is probably the maximum to be expected for the industrially important class of paraffinic lubricating oils. Highly refined mineral oils (compounds 4 and 5) approach the level of stability of octacosane (T_D = 630° to 640° F.).

Hydrocarbons are believed to decompose by a free radical chain mechanism (*10*) of the following type:

$$R\cdot + R'\text{-}CH_2\text{-}CH_2R'' \rightarrow R\text{-}H + R'\text{-}\underset{\cdot}{C}H\text{-}CH_2\text{-}R''$$

$$R'\text{-}CH\text{-}CH_2\text{-}R'' \rightarrow R'CH{=}CH_2 + R\cdot''$$

Branched paraffins should be less stable than octacosane because of steric crowding and greater stability of radicals resulting from cleavage at a branched rather than at an unbranched carbon. The effect of steric crowding is shown by two tetraalkylmethanes (compounds 2 and 3) which decrease in stability as the substituent groups increase in size. In a tetraalkylsilane (compound 6), steric crowding is relieved by the large size of the silicon atom, and the silane has a stability (T_D = 663° F.) equivalent to that of octacosane.

In an aromatic molecule, such as *p*-quaterphenyl, the strengths of both the C—H (102 kcal.) and the aromatic C—C (~120 kcal.) bonds are, because of resonance and hybridization, higher than the corresponding bonds, 99 and 83 kcal., respectively, of a paraffin. The C_6H_5—C_6H_5 bond in *p*-quaterphenyl is also strengthened by conjugation between rings. More energy is thus required to decompose an aromatic than an aliphatic compound by bond rupture, and a free radical chain decomposition is less favorable in aromatic than in aliphatic compounds. Steacie (*15*) has shown the rates of abstraction of H atoms by methyl radicals to be 12 times as great for an aliphatic secondary hydrogen as for a benzene hydrogen. The upper stability limit of aromatic hydrocarbons, represented by *p*-quaterphenyl (T_D = 851° F.) (compound 7), is 200° F. above the best aliphatics.

The two ferrocene derivatives (compounds 9 and 10) are included with the hydrocarbons because of their close comparative stability to octacosane. Since there is only a small difference between an aliphatic substituted ferrocene (T_D= 624° F.) (compound 9) and an aromatic substituted ferrocene (T_D = 662° F.) (compound 10), it appears unlikely that a derivative of ferrocene will be found with a thermal stability higher than that of a normal alkyl hydrocarbon such as octacosane.

Esters. Esters are commercially the most important class of synthetic lubricants. Bis(2-ethylhexyl) sebacate (T_D = 543° F.) is the base stock for MIL-L-7808 lubricants, a 250° to 350° F. application. This ester (compound 13, Table IV) has a 119° F. lower stability than the highest paraffinic hydrocarbon (compound 1). It replaces hydrocarbons in certain applications, notwithstanding its lower T_D, because it possesses some desired properties lacking in petroleum lubricants which are not discussed here.

All esters with β-hydrogen atoms, such as bis(2-ethylhexyl) sebacate, which have been tested (compounds 12, 13, 30-*o*, 30-*m*, 30-*p*, 31-*o*, 31-*m*, and 31-*p*) had decomposition points in the range 505° to 543° F. At temperatures much

Table II. Useful Life, in Hours for 10% Decomposition

No.	Compound	Metal	Decompn., Pt., ° F.	E', Kcal./Mole	Application Temp., ° F. 425	500	600	800
13	Bis(2-ethylhexyl) sebacate	. . .	543	53.1	91,000	1,400	14	. . .
13	Bis(2-ethylhexyl) sebacate	52–100 steel	441	27.4	240	24	. . .	. . .
25	Propane-1,1,1-trimethylol triheptanoate	. . .	603	67.8	15×10^6	65,000	140	. . .
25	Propane-1,1,1-trimethylol triheptanoate	52–100 steel	493	27.1	980	120	12	. . .
11	Bis(1-methylcyclohexyl) sebacate	. . .	623	59.9	13×10^6	86,000	528	. . .
11	Bis(1-methylcyclohexyl) sebacate	52–100 steel	563	45.3	79,000	2,300	. . .	. . .
4	Highly refined paraffinic mineral oil	. . .	640	60.5	. . .	260,000	1,300	0.48
6	Dodecyl-tris(tetradecyl)silane	. . .	663	65.7	. . .	960,000	2,300	0.48
91	Dow Corning 710 silicone	. . .	732	71.4	. . .	. . .	96,000	7.2
42	*m*-Bis(*m*-phenoxyphenoxy)benzene	. . .	848	63.8	. . .	. . .		1,100

Table III. Hydrocarbons

No.	Compound	Decompn.. Pt., ° F	E', Kcal./Mole	A', Mm. Hg/Sec.
1	Octacosane[a]	662	57.6	2×10^{18}
2	11-Ethyl-11-methylpentacosane[b]	628	67.6	6×10^{22}
3	8-Amyl-8-hexylhexadecane[b]	587	ca. 64	ca. 2×10^{22}
4	Highly refined paraffinic mineral oil MLO-5731[c]	640	60.5	6×10^{19}
5	Highly refined naphthenic mineral oil MLO-7055[c]	630	ca. 60	ca. 6×10^{19}
6	Dodecyl-tris(tetradecyl)silane[c]	663	65.7	2×10^{21}
7	*p*-Quaterphenyl[a]	851	ca. 65	ca. 5×10^{17}
8	*p*-(4-Cyclohexylcyclohexyl)phenyl phenyl ether	659	57.2	2×10^{18}
9	1,1′-Didecylferrocene[c]	624	54.5	9×10^{17}
10	2-Biphenylylferrocene[c]	ca. 662	ca. 53	ca. 7×10^{16}

[a] Eastman Kodak Co. [b] N. Rabjohn, University of Missouri. [c] Wright-Patterson Air Force Base, Ohio (WADC).

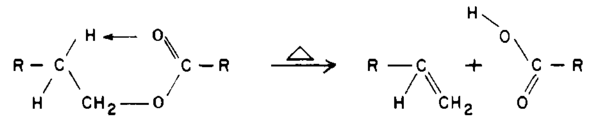
Compounds not marked in this and subsequent tables are of Monsanto origin; otherwise source is indicated.

Compound 4. Pour pt. –5° F.; viscosity cs. 210° F., 21.95; viscosity index 100.3.
Compound 5. Pour pt. –25° F.; viscosity cs. 210° F., 5.65; viscosity index 61.3.

Table IV. Sebacate Esters

No.	Compound	Decompn., Pt., ° F.	E', Kcal./Mole	A', Mm. Hg/Sec.
11	Bis(1-methylcyclohexylmethyl) sebacate	623	59.9	7×10^{19}
12	Dioctyl sebacate	539	52.0	4×10^{16}
13	Bis(2-ethylhexyl) sebacate	543	53.1	1×10^{19}
14	Dibenzyl sebacate	565	67.0	7.4×10^{23}
15	Bis(2,2-diethylpentyl) sebacate	577	57.5	9.5×10^{19}
16	Bis(2,2-dimethylpentyl) sebacate	582	ca. 56	ca. 2×10^{19}
17	Diphenyl sebacate	ca. 533	ca. 46	ca. 4×10^{16}
18	Di-7-norbornyl sebacate	ca. 560	...	...

above 500° F., esters of this type decompose too rapidly from the effects of heat alone to be useful fluids. Esters of alcohols with β-hydrogen atoms decompose thermally to a carboxylic acid and an olefin, probably by a quasi six-membered ring transition state (2) involving the β-hydrogen atom.

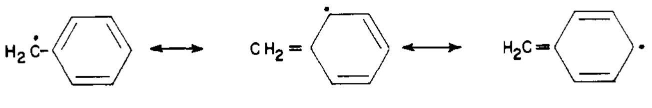


When this reaction path is blocked, as in esters of alcohols without β-hydrogen atoms, the thermal stability limit can be raised as much as 80° F. as shown by bis(1-methylcyclohexylmethyl) sebacate (compound 11), (T_D = 623° F.). These esters approach hydrocarbons in thermal stability and they probably decompose also by a free radical mechanism. If so, 620° to 640° F. is probably the highest stability to be expected for esters of long-chain aliphatic acids.

Esters without β-hydrogen atoms on the alcohol moiety can be prepared from several distinct types of alcohols. The following section describes thermal stabilities of esters of these different kinds of alcohols.

Esters of monohydric alcohols having three alkyl groups on the β-carbon are most closely related structurally to bis(2-ethylhexyl) sebacate in the no β-hydrogen class. The 2,2-dialkylcarbinyl esters (T_D = 577° to 582° F.), (compounds 15 and 16) are 35° F. more stable than bis(2-ethylhexyl) sebacate but are 40° to 50° F. less stable than bis(1-methylcyclohexylmethyl) sebacate (compound 11) in which the β-carbon is a member of a cyclohexane ring. The superiority of the latter ester may be due to the greater compactness of the cyclohexyl ring which lessens vibrational energy peaks and to less steric crowding around the quaternary carbon of the cyclic alcohol than in the acyclic alcohol. In the 2,2-dialkylcarbinyl esters (compounds 15 and 16) the ethyl group is essentially equivalent thermally to the methyl group. Packing a quaternary carbon with groups larger than ethyl would progressively lower the thermal stability of this class of compounds.

The ester (compound 14) of benzyl alcohol, an alcohol in which the β-carbon atom is part of a benzene ring, is better thermally by 25° F. than the primary or secondary alkylcarbinyl esters (compounds 12 and 13), but lower by 17° to 58° F. than the tertiary alkylcarbinyl esters (compounds 11, 15, and 16). The stability of the benzyl ester may be lower because of the tendency to dissociate into a slightly stabilized resonating benzyl radical



which weakens the CH_2—O link. Here resonance contributes in a small way to instability, by stabilizing a decomposition product.

It was thought that the 7-norbornyl ester (compound 18) would have excellent thermal stability because of Bredt's rule which states that a bridgehead atom cannot participate in a double bond. Although this ester (T_D = 560° F.), was indeed more stable than bis(2-ethylhexyl) sebacate, steric strain in the norbornane structure may have prevented attainment of the stability level of bis(1-methylcyclohexyl) sebacate.

Instead of alkyl groups the β-hydrogen atoms of the alcohol may also be replaced by fluorine atoms. Bis(1,1,5-trihydroperfluoroamyl) diphenate and bis(1,1,7-trihydroperfluoroheptyl) 3-methyl glutarate (Table V), are equivalent in thermal stability to the better tertiary alkylcarbinyl esters (compounds 12, 20, 11, and 21). Of these two fluorinated esters, the glutarate is lower in thermal stability because of the tendency to revert to the anhydride.

Neopentylpolyol esters (Table VI) are a fourth type of esters having no β-hydrogen atoms on the alcohol moiety. Neopentylpolyols important in this class are 2,2-dialkyl-1,3-propanediol, 1,1,1-trimethylolpropane, and pentaerythritol. Esters of the later two polyols are active candidates for the MIL-L-9236 specification, an application 75° to 175° F. higher than the MIL-L-7808 specification. These two triol and tetrol esters (compounds 25 and 26) are 40° to 60° F. more stable than bis(2-ethylhexyl) sebacate (compound 13), but 20° to 38° F. less stable than the most stable sebacate ester (compound 11). In the two diol esters

Table V. Fluorinated Esters

No.	Compound	Decompn., Pt., ° F.	E', Kcal./Mole	A', Mm. Hg/Sec.
19	Bis(1,1,5-trihydroperfluoroamyl) diphenate[a]	621	ca. 49	ca. 8×10^{15}
20	Bis(1,1,7-trihydroperfluoroheptyl) 3-methylglutarate[a]	592	ca. 60	ca. 3×10^{20}
21	1-Methylcyclohexylmethyl 4-biphenylcarboxylate	616	53.0	3.5×10^{17}

[a] E.I. du Pont de Nemours & Co.

Table VI. Neopentylpolyol Esters

No.	Compound	Decompn., Pt., ° F.	E', Kcal./Mole	A', Mm. Hg/Sec.
22	2,2-Dimethyl-1,3-propanediol dilaurate	612	57.9	3×10^{19}
23	2-Butyl-2-ethyl-1,3-propanediol dilaurate	592	57.6	5×10^{19}
24	2-Cyclopentamethylene-1,3-propanediol dilaurate	615	52.8	3×10^{17}
25	Propane-1,1,1-trimethylol triheptanoate	ca. 603	67.8	2×10^{23}
26	Pentaerythritol tetrahexanoate	585	56.4	3×10^{19}

(compounds 22 and 23) thermal stability drops as the R group increases in size—another example of steric crowding which weakens the C—C bond. A higher stability level for cyclic structures *vs.* acyclic structures is further demonstrated by comparison of compounds 23 and 24.

In addition to aliphatic esters of alcohols without β-hydrogen atoms, aromatic and hydroaromatic esters (Table VII) were studied. Tertiary alkylcarbinyl phthalates (compounds 27 and 32) are 80° to 90° F. higher in stability than the corresponding normal alkyl esters (compound 30) for reasons previously presented.

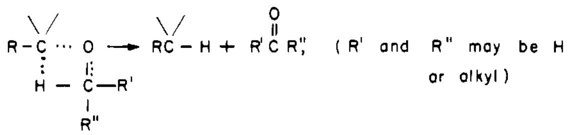
It was surprising, that *o*-phthalates (Table VII) showed such a small lowering of thermal stability as compared with the *m*- and *p*-phthalates of the same alcohol (compounds 27-*o*-,*m*-,*p*- and 30-*o*-,*m*-,*p*-, Table VII). The *m*- and *p*-phthalates of the same alcohol are essentially equivalent in stability (compounds 27-*m*-,*p*-, 28-*m*-,*p*-, and 31-*m*-,*p*-). The small trend to lower stability in the *o*-phthalates and *o*-hexahydrophthalates (compounds 27-*o*-, 28-*o*-, 30-*o*-, and 31-*o*-) *vs.* the *m*- and *p*-phthalates may result from either ease of anhydride formation or higher acid strength, or both. This tendency appears to be exaggerated in the case of the pyromellitic ester (compound 29). Pyromellitic acid is a much stronger acid than *o*-phthalic and esters of strong acids in numerous instances are less stable than esters of weak acids.

The hexahydrophthalates have a higher stability than the corresponding phthalates, probably because the hexahydrophthalic acids are weaker than phthalic acids. *m*- and *p*-hexahydrophthalates (compounds 28-*m*-, and 28-*p*-) have the highest stability of any ester tested, again suggesting the greater stability of a cyclohexane ring over an alkane chain.

Amides. It is interesting to compare amides (Table VIII) with esters, in an attempt to show if inhibition of olefin elimination would improve thermal stability to the same degree as it did with esters.

The decomposition of the *N,N*-dialkyl amides falls between the normal alkyl esters (compounds 13, 33, and 35) and the most stable tertiary alkylcarbinyl esters (compounds 11), and only slightly lower than neopentylpolyol esters (Table VI). The small difference of 28° F. between compounds 33 and 34 would suggest that if olefin elimination is the degradation mechanism for amides, it is not the only one operating at this temperature level.

Ethers. Primary and secondary aliphatic ethers decompose to a paraffin and an aldehyde or ketone. Decomposition to produce a carbonyl group is a lower energy path than for the production of an alcohol and may proceed via either a four-center transition state,



or a free radical chain decomposition favored by the ease of radical attack at the α-carbon of an ether,

$$RCH_2OCHR'R'' + RCH_2\cdot \rightarrow RCH_2O\underset{\cdot}{C}R'R'' + RCH_3$$

$$RCH_2O\underset{\cdot}{C}R'R'' \rightarrow RCH_2\cdot + O{=}CR'R''$$

Both of these decomposition mechanisms, which may proceed simultaneously in ether decompositions, should require more energy than decomposition of an ester by the quasi six-membered ring transition state, but less than that required for free radical decomposition of a hydrocarbon.

The predicted order of stability was observed. Bis(tetradecyl)ether (compound 36, Table IX) (T_D = 554° F.), has a decomposition point 15° F. higher than dioctyl sebacate (compound 12), but 108° F. lower than octacosane (compound 1), and 175° F. lower than a methyl-substituted aromatic ether (compound 45).

An attempt to improve the stability of an ether by replacing the α-hydrogen atoms with alkyl groups would be expected to fail because of the ease of elimination of the resulting tertiary alkyl group as an olefin. However, when one of the α-carbon atoms is part of a benzene ring so that decomposition proceeds by a different mechanism, the

Table VII. Phthalates

		Ortho			Meta			Para		
No.	Compound	Decompn., Pt., ° F. ° F.	E', Kcal./ Mole	A', Mm. Hg/ Sec.	Decompn., Pt., ° F. ° F.	E', Kcal./ Mole	A', Mm. Hg/ Sec.	Decompn., Pt., ° F. ° F.	E', Kcal./ Mole	A', Mm. Hg/ Sec.
27	*o*-, *m*-, *p*-Bis(1-methylcyclohexylmethyl) phthalate	587	50.2	1×10^{17}	593	45.3	1×10^{15}	596	49.8	5×10^{16}
28	*o*-, *m*-, *p*-Bis(1-methylcyclohexylmethyl) hexahydrophthalate	613	54.7	2×10^{18}	642	64.6	2×10^{21}	648	64.0	8×10^{20}
29	Tetrakis(1-methylcyclohexylmethyl) pyromellitate	497	48.7	2×10^{18}	...	...	...	...	...	...
30	*o*-, *m*-, *p*-Dioctyl phthalate	506	52.4	3×10^{19}	514	40.5	4×10^{18}	516	52.6	2×10^{19}
31	*o*-, *m*-, *p*-Dioctyl hexahydrophthalate	516	46.4	7×10^{16}	530	52.8	1×10^{19}	533	53.7	3×10^{19}
32	Dineopentyl phthalate	595	ca. 54.5	ca. 3×10^{18}	...	...	...	...	...	...

Table VIII. Amides

No.	Compound	Decompn., Pt., ° F.	E', Kcal./Mole	A', Mm. Hg/Sec.
33	*N,N,N',N'*-tetrabutylsebacamide	560	ca. 44	ca. 9×10^{14}
34	*N,N'*-Dimethyl-*N,N'*-bis(1-methylcyclohexylmethyl)sebacamide	588	ca. 49	ca. 3×10^{16}
35	1,1-Dibutyl-3,3-dioctylurea	567	47.5	2×10^{16}
13	Bis(2-ethylhexyl) sebacate	543	53.1	1.5×10^{16}
11	Bis(1-methylcyclohexylmethyl) sebacate	623	59.9	9.5×10^{19}

Table IX. Aliphatic Ethers

No.	Compound	Decompn., Pt., ° F.	E', Kcal./Mole	A', Mm. Hg/Sec.
36	Bis(tetradecyl) ether	554	49.9	3×10^{17}
42	*m*-Bis(*m*-phenoxyphenoxy)benzene	848	63.8	2×10^{17}
45	*m*-Tolyl *p*-phenoxyphenyl ether	729	ca. 51.6	2×10^{15}
39	Bis[*p*-(*p*-methoxyphenoxy)phenyl] ether	573	46.6	8×10^{15}
40	Diphenoxy-*p*-xylylene	430	30.3	2×10^{19}

stability is raised 20° F. as shown by a methyl aryl ether (compound 39). The low stability of diphenoxy-*p*-xylylene (compound 40), (T_D = 430° F.), a phenyl benzyl ether, indicates a low-energy decomposition path probably to yield *p*-quinodimethane. When both α-carbon atoms are replaced by phenyl groups, stability is raised by 294° F. as shown by the unsubstituted aromatic ether (compound 42). Stability of aromatic ethers is probably limited by the strength of the C—H bond since diphenyl ether when heated at 840° F. loses hydrogen to form dibenzofuran among other products.

Unsubstituted aromatic ethers (Table X) rank among the most stable of large organic molecules. They are equaled only by aromatic amines, aromatic hydrocarbons, and aromatic triazines, all of which have strong resonating structures. A comparison of compounds 41, 42, and 43 shows that the meta- and para-linked ethers are of equal thermal stability and suggests that the ortho-linked ether may be slightly less stable.

Having established the thermal stability of unsubstituted aromatic ethers, it became of interest to study the thermal stability of substituted aromatic ethers. These data should be applicable to other classes of compounds, since the thermal stability of a substituent on a stable molecule such as a polyaromatic ether should be an indication of its stability when attached to a phenyl ring in other molecules such as polyaromatics.

Alkyl-substituted ethers (Tables XI and XII) have stabilities over 100° F. lower (compounds 42 and 46) than unsubstituted ethers because of a lower energy—i.e., free radical—decomposition path. Increasing the number of substituents causes a steady decline in thermal stability, mono > di > tetra because of more decomposition sites (compounds 46, 47, and 48). Stability also decreases as the chain length of the alkyl substituent is increased (compounds 50, 52, and 53) until it approaches the stability of hydrocarbons (compounds 1 and 56). The first major drop in stability occurs in going from the ethyl to the propyl group (compounds 50, 51, and 52). Cyclic structures are more stable than equivalent normal alkyl chains (compounds 49 to 52).

Table X. Unsubstituted Aromatic Ethers

No.	Compound	Decompn., Pt., ° F.	E', Kcal./Mole	A', Mm. Hg/Sec.
41	*m*-(*m*-Phenoxyphenoxy)phenyl *p*-phenoxyphenyl ether	840	69.6	2×10^{19}
42	*m*-Bis(*m*-phenoxyphenoxy)benzene	848	63.8	2×10^{17}
43	*o*-Bis(*m*-phenoxyphenoxy)benzene	822	62.7	2×10^{17}

Table XI. Methyl-Substituted Aromatic Ethers

No.	Compound	Decompn., Pt., ° F.	E', Kcal./Mole	A', Mm. Hg/Sec.
44	*o*-Tolyl *p*-phenoxyphenyl ether	730	ca. 50	ca. 6×10^{14}
45	*m*-Tolyl *p*-phenoxyphenyl ether	729	ca. 52	ca. 2×10^{15}
46	*p*-Tolyl *p*-phenoxyphenyl ether	732	ca. 50	ca. 6×10^{14}
47	*p*-Bis(*m*-toloxy)benzene	712	53.9	2×10^{16}
48	*p*-Bis(3,5-dimethylphenoxy)benzene	703	56.4	2×10^{17}

A number of miscellaneous substituents are listed in Table XIII. The *p*-benzyl linkage on a benzene ring is just as stable as the *p*-methyl linkage (compounds 47, Table XI; 57, Table XIII). It is 62° F. more stable than the ethyl phenyl linkage (compounds 57 and 58) which may have a low-energy path of decomposition with the elimination of styrene or stilbene. para-Chlorination of the benzyl group greatly (194° F.) lowers stability (compounds 57 and 60). The cyano substituent is of the same order of stability as the chloro derivatives (compounds 59 and 87). The great instability which the trifluoromethyl group (compound 61) imparted to the molecule was not expected. As expected, from previous data on *p*-quaterphenyl and unsubstituted polyaromatic ethers, bis(*p*-phenylphenyl) ether (compound 62) has the same level of stability as polyaromatics and polyaromatic ethers.

Amines. With polyaromatic ethers as a class showing extreme thermal stability, it was of interest to study some nitrogen analogs (Table XIV).

The nitrogen linkage between phenyl groups is as thermally stable as an oxygen link, as shown by the high

Table XII. Alkylated Aromatic Ethers

No.	Compound	Decompn., Pt., ° F.	E', Kcal./Mole	A', Mm. Hg/Sec.
42	*m*-Bis(*m*-phenoxyphenoxy)benzene	848	63.8	2×10^{17}
49	*p*-Cyclohexylphenyl *p*-phenoxyphenyl ether	706	56.2	1×10^{17}
50	*p*-Bis(*p*-toloxy)benzene	721	ca. 55	ca. 4×10^{16}
51	*p*-Bis(*p*-ethylphenoxy)benzene	720	ca. 44	ca. 6×10^{12}
52	*p*-Bis(*p*-propylphenoxy)benzene	670	ca. 66	ca. 1×10^{21}
53	*p*-Bis(*p*-octylphenoxy)benzene	639	57.7	6×10^{18}
54	*p*-Bis(*p*-*tert*-butylphenoxy)benzene	700	59.0	2×10^{18}
55	*p*-Bis(*p*-isopropylphenoxy)benzene	719	ca. 55	ca. 3×10^{16}
56	*m*-Pentadecylphenyl phenyl ether	650	64.0	7×10^{20}

Table XIII. Miscellaneous Substitution on Aromatic Ethers

No.	Compound	Decompn., Pt., ° F.	E', Kcal./Mole	A', Mm. Hg/Sec.
57	Bis(*p*-benzylphenyl) ether	721	59.4	9×10^{17}
58	*p*-Phenoxy-1,2-diphenylethane	659	ca. 60	ca. 2×10^{19}
59	*p*-Bis(*p*-cyanophenyl)benzene	756	...	...
60	*p*-(*p*-Chlorobenzyl)phenyl phenyl ether	527	ca. 45	ca. 1×10^{16}
61	Bis[*p*-(*m*-trifluoromethylphenyoxy)phenyl]ether	ca. 514	...	...
62	Bis(*p*-phenylphenyl)ether	858	...	...

Table XIV. Aromatic Amines

No.	Compound	Decompn., Pt., ° F.	E', Kcal./Mole	A', Mm. Hg/Sec.
63	*N,N'*-Diphenyl-*p*-phenylenediamine[a]	ca. 509	ca. 28	ca. 3×10^{9}
64	*N,N'*-Diphenyl-*N,N'*-dimethyl-*p*-phenylenediamine	620	53.3	3×10^{17}
65	*N,N,N',N'*-Tetraphenyl-*p*-phenylenediamine	856	ca. 71	ca. 2×10^{19}
66	*N,N'*-Diphenyl-benzidine	761	62	1×10^{18}
67	*m*-Phenoxyphenyl *m*-aminophenyl ether	774	ca. 57	ca. 1×10^{16}

[a] Matheson, Coleman, and Bell.

decomposition point, 856° F., of a triarylamine (compound 65). Since both aromatic amines and ethers are equivalent in stability to *p*-quaterphenyl (compound 7) (T_D = 851° F.), the weak points in these molecules are not the resonance hybridized links between phenyl rings, but the C—H bonds in the benzene ring.

From bond energies, N—H = 93 kcal. per mole as compared to $N—CH_3$ = 68 kcal. per mole, it would be predicted that *N,N'*-diphenyl-*p*-phenylenediamine (compound 63) would have a higher stability than *N,N'*-diphenyl-*N,N'*-dimethyl-*p*-phenylenediamine (compound 64). Compound 63, however, can decompose by a low-energy path to yield *N,N'*-diphenyl-*p*-quinonediimine and has a decomposition point of 509° F. as compared with 620° F. for compound 64. When the $N—CH_3$ bond is replaced by the more stable $N—C_6H_5$ bond, as in *N,N,N',N'*-tetraphenyl-*p*-phenylenediamine (compound 65), the decomposition point is raised to 865° F. This is a second example of the striking increase (347° F.) in thermal stability, which can result by blocking a low-energy decomposition mechanism. That the N—H bond is inherently stable is shown by the decomposition point of 761° F. for *N,N'*-diphenylbenzidine (compound 66), which because of the biphenyl link cannot decompose to give a quinonediimine as does compound 63, and by the decomposition point of 774° for the primary amine, compound 67.

Inorganic Esters. The class of inorganic esters (Table XV) includes several commercial hydraulic fluids which are based on silicates, siloxanes, and phosphates. Compared to a typical organic ester, bis(2-ethylhexyl) sebacate, the silicates, siloxanes, and also the alkyl borates have decomposition points 100° F. higher, while alkyl phosphates have decomposition points as much as 140° F. lower (compounds 12, 69, 72, 75, and 76).

If the silicate and borate decompositions took place through an intramolecular hydrogen bridge transition state involving the β-, γ-, or δ-hydrogen and the inorganic ester oxygen, then a higher activation energy would be required for decomposition than that involving the more polarized carbonyl oxygen of an aliphatic ester. However, some preliminary data indicate that a free radical mechanism is the dominant mechanism in the decomposition of normal alkyl silicates and borates, perhaps involving rupture of $CH_2—O$ bonds or of C—H bonds of the α-carbon atom.

This decomposition path cannot be blocked by simple structural modifications. Therefore, silicate and borate esters from alcohols with no β-hydrogen atoms show a small increase (30° to 40° F.) in thermal stability as compared to their normal esters (compounds 72, 73, 74, and 75). This is in contrast to the much larger (80° F.) increase in thermal stability shown by a similar comparison of aliphatic carboxylic esters in which a low-energy path of decomposition was blocked (compounds 11 and 13).

The fact that the decomposition points of the largely aliphatic 1-methylcyclohexylmethyl borate (compound 73), (T_D = 692° F.), and 1-methylcyclohexylmethyl silicate (compound 74), (T_D = 682° F.), are greater than octacosane is further evidence for the greater stability of cyclic over acyclic structures.

The orthosilicates (compound 75) and disiloxanes (compound 76) are essentially equivalent in stability, which would be predicted from their analogous structures.

Aromatic silicates and borates are up to 130° F., more stable than analogous aliphatic esters (compounds 70, 71, 72, and 73) because the phenyl rings are inherently more stable toward free radical decomposition than alkyl chains and the resonance-stabilized aromatic C—O bond is stronger than the aliphatic C—O bond.

A normal alkyl phosphate should decompose by a mechanism similar to that of aliphatic carboxylic esters. Since the P=O bond in an alkyl phosphate is more ionic in character than the carbonyl group in a carboxylate, its contribution to a low-energy, intramolecular, hydrogen-bridge transition state is greater and the decomposition temperature is lowered by 140° F. Furthermore, the decomposition of an alkyl phosphate yields phosphoric acid, an acid sufficiently strong to catalyze the decomposition of unchanged phosphate.

Phenyl Derivatives of Elements of Groups III A, IV A, V A, VI A, and VII A. Thermal stabilities of a series of compounds (Table XVI) of the type $(C_6H_5)_nM$ were measured to show the variation in stability of the bond C—M as a function of the position of M in the periodic table. Any decrease in stability below that of the phenyl group, as exemplified by *p*-quaterphenyl (T_D = 851° F.), should be due either directly to a lower bond strength or to a decomposition path related to the specific nature of M or the C—M bond.

In an attempt to separate these effects, decomposition points were plotted in Figure 3 as a function of the C—M bond length. Within a periodic group, as shown by the group V A elements, thermal stability is inversely proportional to bond length. In the V A series (Figure 3) the $C_6H_5—M$ bond length varies from 1.4 A. for *N,N,N',N'*-tetraphenyl-*p*-phenylenediamine to 2.30 A. for triphenylbismuthine and the T_D decreases from 856° to 456° F. If the assumption is made that bond strength is also inversely proportional to bond length (*12*), then in this class of compounds, thermal stability is directly related to the C—M bond strength within a group of elements, M.

The influence of the nature of the central atom, M, on thermal stability is also suggested in Figure 3. Although the IV A group elements—silicon, germanium, and tin—are slightly larger as well as slightly lower in electronegativity

Table XV. Inorganic Esters

No.	Compound	Decompn., Pt., ° F.	E', Kcal./Mole	A', Mm. Hg/ Sec.
68	Triphenyl phosphate	≧793	. . .	. . .
69	Trioctyl phosphate	ca. 383	. . .	. . .
70	Tri(*m*-phenoxyphenyl) borate	829	59.7	2×10^{16}
71	Tetraphenyl orthosilicate	844	ca. 53.8	ca. 6×10^{15}
72	Trisdodecyl borate	660	63.8	4×10^{20}
73	Tris(1-methylcyclohexylmethyl) borate	692	ca. 64	ca. 9×10^{19}
74	Tetra(1-methylcyclohexylmethyl) orthosilicate	682	65.1	4×10^{20}
75	Tetra(2-ethylhexyl) orthosilicate	638	67.5	2×10^{22}
76	Hexa(2-ethylbutoxy)-disiloxane	627	59.4	5×10^{19}

Table XVI. Thermal Stability of Compounds of the Type $(C_6H_5)_mM$ as a Function of Bond Length

No.	Compound	*M*	Decompn., Pt., ° F.	*E*′, Kcal./Mole	*A*′, Mm. Hg/Sec.	Bond Length, A.[a]
7	*p*-Quaterphenyl	. . .	851	ca. 65	ca. 5×10^{17}	1.50
77	Triphenylboron[c]	B	ca. 529	. . .	. . .	1.56
78	Tetraphenylmethane	C	≧777	. . .	. . .	1.47
79	Tetra-*p*-biphenylylsilane[d]	Si	810	ca. 58	ca. 9×10^{15}	1.87
80	Tetraphenylgermanium	Ge	733	ca. 49	ca. 3×10^{14}	1.98
81	Tetraphenyltin[e]	Sn	659	67.7	2×10^{21}	2.18
65	*N,N,N′,N′*-tetraphenyl-*p*-phenylenediamine	N	856	ca. 71	ca. 2×10^{19}	1.40
82	Triphenylphosphine[f]	P	≧697	. . .	. . .	1.70[b]
83	Triphenylphosphine oxide	P	764	57.2	3×10^{16}	1.70[b]
84	Triphenylarsine[f]	As	587	57.6	6×10^{19}	1.95
85	Triphenylstibine	Sb	513	50.5	4×10^{18}	2.20
86	Triphenylbismuthine[f]	Bi	448	52.6	9×10^{20}	2.30
62	Bis(*p*-phenylphenyl) ether	O	857	. . .	. . .	1.36
87	*p*-Bis(*p*-chlorophenoxy)benzene	Cl	769	ca. 53	ca. 2×10^{15}	1.70
88	*p*-Bis(*p*-bromophenoxy)benzene	Br	728	ca. 60	ca. 8×10^{17}	1.85

[a] Except as noted bond lengths were selected from (*8*).
[b] Sum of covalent atomic radii.
[c] Heyl & Co., Chem. Pharm. Fabrik.
[d] WADC.
[e] Matheson, Coleman, and Bell.
[f] Eastman Kodak Co.

than the V A group elements—phosphorus, arsenic, and antimony—the phenylated compounds of the IV A class are more stable than their V A analogs. This is not an anomaly because in the phenylated IV A group compounds, the covalent C_6H_5—M bonds have sp^2-sp^3 hybridization which is stronger (*9*) than the sp^2-p hybridization of the bonds of the V A group compounds. The exception in the IV A series is tetraphenylmethane (T_D = 777° F.) which has a 33° F. lower T_D than tetra-*p*-biphenylsilane (T_D = 810° F.). Steric crowding and the possibility of forming a stable triphenylmethyl radical may both contribute to this lower T_D.

Triphenylphosphine oxide (T_D = 764° F.) is thermally more stable than triphenylphosphine (T_D = 697° F.) because the sp^2-sp^3 covalent bonds of the oxide are more stable bonds than the sp^2-p covalent bonds of triphenylphosphine.

Thermal stability measurements indicate that the C_6H_5—C_6H_5 bond in *p*-quaterphenyl, the C_6H_5—N bond in aromatic amines, and the C_6H_5—O bond in aromatic ethers are at least as strong as and probably stronger than the aryl carbon-hydrogen bond. The C_6H_5—C_6H_5 bonds in *p*-quaterphenyl have sp^2-sp^2 hybridization and are further stabilized by resonance interaction between benzene rings. The C_6H_5—N and the C_6H_5—O bonds in aromatic amines and ethers may also have sp^2-sp^2 hybridization (based on bond angles of 120° to 130° in these compounds) with further stabilization by resonance interaction with the phenyl ring. The fact that triphenylboron has a low T_D, although the C_6H_5—B bonds have strong sp^2-sp^2 hybridization, may be due to the possibility that it can initiate decomposition by electrophilic attack on a phenyl ring.

The relatively low change in decomposition point with bond length of the halogen derivatives may be rationalized by assuming that hydrogen halide is eliminated, possibly intramolecularly, at a lower energy level than by direct fission of the bond. The larger size of the bromine atom and lower electronegativity as compared to chlorine should contribute to a lower stability for organic bromine compounds in comparison with their chlorine analogs.

Of the elements studied, only oxygen, nitrogen, and possibly silicon can be used to link phenyl groups in large molecules without loss of stability.

Silanes and Silicones. Aliphatic silanes (Table XVII) have the same level of thermal stability (compounds 1, 89, and 90) as the better hydrocarbons and must decompose by the same free radical mechanism. Aromatic silanes are more stable by 147° F. than aliphatic silanes (compounds 79 and 89), and approach the stability of aromatic hydrocarbons.

Silicones are hybrids of silanes and siloxanes. Both silicones tested, Dow Corning 550 and 710 (compounds 91 and 92), contain methyl groups. Because of the presence of an aliphatic C—H bond they are less stable than aromatic silanes and their decomposition points of 732° F. are in line with the methyl-substituted aromatic ethers (compound 46). These silicones are more stable than aliphatic silanes and siloxanes because the long alkyl chains of the latter are less stable than the small methyl group of the silicones, as was shown in the alkyl-substituted aromatic ethers. Also, the long backbone chain of a silicone consists of Si—O bonds which, with an energy of 106 kcal., are stronger than the C—C (83 kcal.) or C—Si (60 kcal.) bonds of a silane.

Heterocyclics. Two heterocyclic rings, pyridine and 1,3,5-triazine, are present in the compounds tested in this class (Table XVIII). By calculations from heats of combustion (*16*), pyridine has been shown to have the same order of resonance stability as benzene, or slightly greater. The symmetrical triazine ring should also be at least as stable as benzene, since it should have a highly resonating stable nucleus and it has fewer ring hydrogen atoms than benzene. This is borne out by compound 96, which has the highest stability (T_D = 867° F.), of any compound tested and is comparable to the *N,N,N′,N′*-tetraphenyl-*p*-phenylenediamine (compound 65, T_D = 856° F.).

The low stabilities of compounds 93, 94, and 95 suggest that electron-donating substituents on pyridine and triazine heterocyclic rings lower the stability of the substituted heterocyclic.

Sulfones-Ketones. Comparison of compounds 97 and 99 (Table XIX) suggests that aromatic sulfones and aromatic ketones have about the same order of stability. The fact that in compound 97 the two phenylsulfonyl groups are substituted on the same benzene ring may contribute to the small T_D difference of 17° F. between the two compounds.

Compound 98 has a low thermal stability because it can undergo a low-energy, aldol-type condensation with elimination of water, as does acetophenone in forming dypnone.

By a comparison of compound 99 (T_D = 745° F.) with compound 41 (T_D = 840° F.) it seems reasonable to conclude that the C_6H_5—O bond is appreciably stronger than the C_6H_5—CO bond.

Stability in Presence of 52-100 Steel. Hydraulic fluids and lubricants must possess adequate thermal stability in the presence of certain metals if they are to be commercial materials. Several compounds representing different chemical structures have been checked in the thermal stability test in the presence of 52-100 steel. The effect of 52-100 steel on these structures is shown in Table XX.

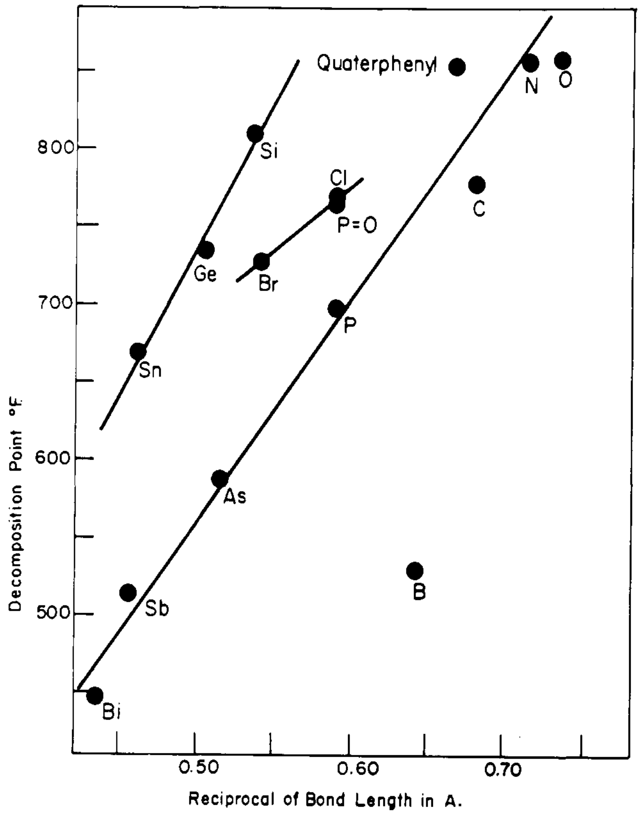


Figure 3. Decomposition point as a function of the C_6H_5-M bond length in compounds of the type $(C_6H_5)_mM$

The thermal stability of hydrocarbons, silicones, silanes, aromatic ethers, and aromatic amines is essentially unaffected by 52-100 steel. Esters as a class have a lower T_D by 60° to 100° F. Lowering of thermal stability in carboxylic and phosphoric acid esters may be due to unstable iron carbonyl-type structures resulting from coordination with the iron of the polarized carbonyl and/or phosphine oxide bonds.

USEFUL LIFE

Thermal stability data can be extrapolated by means of Equation 13 to estimate the useful life of a compound at a given temperature. In Equation 13, t is the time in hours for a compound of density d, molecular weight M, decomposition point T_D ° K, and energy of activation E' to undergo x per cent decomposition at a temperature T ° K

$$t = -\frac{0.0285\,T_D}{M}\log\left(\frac{100-x}{100}\right)$$

$$\text{antilog}\left[5 - 219\,E'\left(\frac{1}{T_D} - \frac{1}{T}\right)\right] \quad (13)$$

In the derivation of this equation the change of density with temperature is neglected, and it is assumed that the mode of decomposition of a compound is unchanged over the temperature range T_D to T, that thermal decomposition is a unimolecular reaction, and that one molecule enters the gas phase per molecule of compound decomposed.

Table XVII. Silanes and Silicones

No.	Compound	Decompn., Pt., ° F.	E', Kcal./Mole	A', Mm. Hg/Sec.
89	Dodecyltris-(tetradecyl)silane[a]	663	65.7	2×10^{21}
90	Tris(*p*-phenoxyphenyl)-dodecylsilane[a]	663	55.2	3×10^{17}
79	Tetra-*p*-biphenylyl-silane[a]	810	ca. 58	ca. 9×10^{15}
91	Dow Corning 710 Silicone[b]	732	ca. 71	5×10^{21}
92	Dow Corning 550 Silicone[b]	ca. 740	...	...

[a] WADC. [b] Dow Corning Corp.

Table XVIII. Heterocyclics

No.	Compound	Decompn., Pt., ° F.	E', Kcal./Mole	A', Mm. Hg/Sec.
93	N^2,N^4,N^6-Triphenylmelamine	ca. 657	...	...
94	2,4,6-Triphenoxy-*s*-triazine	497	34.3	2×10^{12}
95	Bis[*p*-(3-pyridoxy)-phenyl] ether	630	...	...
96	2,4,6-Triphenyl-*s*-triazine	867	ca. 56	5×10^{14}

Table XIX. Sulfones-Ketones

No.	Compound	Decompn., Pt., ° F.	E', Kcal./Mole	A', Mm. Hg/Sec.
97	*m*-Bis(phenylsulfonyl)-benzene	728	58.6	4×10^{17}
98	Bis(*p*-acetylphenyl) ether	351	ca. 32	ca. 6×10^{13}
99	Bis(*p*-benzoylphenyl) ether	745	ca. 50	ca. 3×10^{14}

Table XX. Stability in the Presence of 52–100 Steel

Compound	Decomposition Point, ° F. No metal	Decomposition Point, ° F. 52-100 steel	Difference
Bis(2-ethylhexyl) sebacate	543	441	−102
Bis(1-methylcyclohexylmethyl) sebacate	623	563	−60
Propane-1,1,1-trimethylol triheptanoate	603	493	−110
Octacosane	662	658	−4
Dow Corning Silicone 710	732	727	−5
Tris(3,4-dimethylphenyl) phosphate	718	652	−66
Triphenyl-*p*-biphenylylsilane	799	803	+4
N,N,N',N'-Tetraphenyl-*p*-phenylenediamine	856	860	+4
m-Phenoxyphenyl *p*-phenoxyphenyl ether	802	795	−7

Practical environmental conditions such as temperature, type of metals in contact with fluid, shearing forces, and severity of exposure to oxidation, will of course vary widely in operation and thus affect the actual life. It does not seem unreasonable, therefore, to assume that the calculated useful life (Table II) for some unhibited, commercial and potentially commercial base stock chemicals is the maximum that can be expected. Such calculations are useful as a guide because they indicate peak application levels and trends to be expected in actual performance. The temperature of 425° F. is chosen for some comparisons because military specifications are now being formalized around this temperature. Of the compounds tested, the presence of 52-100 steel showed the most effect on the T_D's of esters (Table XIX) and the useful life calculations on three esters show the magnitude of this effect.

Qualitatively, in useful life, these compounds may be classified in the following order: aromatics > silicones >

silanes > mineral oils > tertiary alkylcarbinyl esters > alkyl esters.

These calculations indicate that of the three esters (compounds 11, 13, and 25), compounds 11 and 25 should show materially better stability performance for a 425° F. application. Compound 11 should show better performance than compound 25 as the application temperature progresses toward 500° F. In the 500° to 600° F. range, mineral oils, silanes, and silicones are adequate and beyond 600° F., only compounds with stability in the range of compound 42 would be suitable.

Credence is added to these data by some laboratory and practical testing. Heating of compounds 11 and 13 in glass at different temperatures, under nitrogen, for 10 hours showed the following per cent viscosity change at 210° F.:

	Compound	
	13	11
Temp., ° F.	Change in Viscosity, % at 210° F.	
446	-0.5	0.0
498	-1.2	-0.6
540	-0.9	-0.4
606	-15.0	+0.3
646	solid	-1.9

Republic Aviation Corp. has reported (*11*) that a polyphenyl ether fluid in a prototype hydraulic system has performed satisfactorily at 800° F. for 25 hours.

Pratt and Whitney Aircraft has obtained an outstanding performance on compound 42 which underwent less than 3% decomposition when run for 100 hours in an endurance bearing rig test at a bearing temperature of 500° F. with a saturated air flow of 0.3 cu. foot per minute and without antioxidant.

Wright Air Development Center (*1*) has run an ester of the type represented by compound 25 for 80 hours, in a jet engine, at an oil temperature of 425° F. and found it to undergo only a small viscosity change.

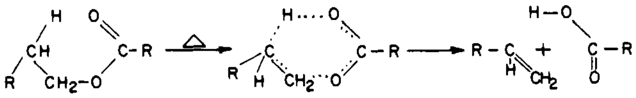
DISCUSSION AND CONCLUSIONS

As an organic compound is heated to higher and higher temperatures, the vibrational energy distributed among the bonds of the molecule increases. In the simple case of a diatomic molecule when vibrational energy becomes equal to bond strength, the molecule will rupture, and the energy of activation of decomposition in Equation 3 will be equal to the bond strength. In more complex molecules, the bond strength of the weakest bond determines the upper limit of the thermal stability of the molecule, if there are no low-energy decomposition paths. The influence of bond strength on thermal stability was well illustrated by the triphenyl derivatives of group VA elements—nitrogen, phosphorus, arsenic, antimony, and bismuth—a series of compounds which has no obvious decomposition path other than bond fission. In the absence of reliable bond strength data, it was assumed that bond strength was inversely proportional to bond length. It was found (Table XVI, Figure 3) that decomposition points decreased as bond length increased from 856° F. for *N,N,N′,N′*-tetraphenyl-*p*-phenylenediamine (compound 65) (C—N = 1.40 A., aliphatic C—N bond strength probably 73 kcal.) to 448° F. for triphenylbismuthine (compound 86) [C—Bi = 2.30 A., C—Bi bond strength in $(CH_3)_3Bi$ = 31 kcal.]. Thus, in the series of compounds $(C_6H_5)_3M$ where the only change was in the C_6H_5—M bond, the thermal stability varied over a 400° F. range. Bond strengths are from (*8*) and bond lengths from (*7*).

The effects on bond strength of resonance and of the type of hybridization of the atoms of the bond were illustrated by *N,N,N′,N′*-tetraphenyl-*p*-phenylenediamine and bis(*p*-phenylphenyl) ether (compound 62, T_D = 862° F.) which have higher stabilities than tetraphenylmethane (compound 78, T_D = 777° F.), although the strengths of the C—N (73 kcal.) and C—O (86 kcal.) bonds are not substantially greater than the C—C (83 kcal.) bond. The high stability of benzene is due to resonance hybridization which transforms the structure from one of alternating single-double bonds to one of six equivalent bonds all of strength equal to about one and one half C—C bonds. Stable, large aromatic molecules must be built up by linking phenyl groups with stable atoms or groups. A single bond between benzene rings forms stable molecules, because this C—C bond has sp^2-sp^2 hybridization which is stronger than ordinary C—C bonds with sp^3-sp^3 hybridization (*9*). *p*-Quaterphenyl, as a result, has a high stability of 851° F. Nitrogen and oxygen atoms form stable links between benzene rings because hybridization of the N—C or O—C bonds is equivalent to the sp^2-sp^2 links in *p*-quaterphenyl and the unshared electron pairs of these atoms can resonate with the ring. The aromatic amine and ether were shown to have stabilities equal to *p*-quaterphenyl. In addition to the single bond and oxygen and nitrogen atoms, it was shown that silicate and borate groups, which can also resonate with the phenyl group, link phenyl groups to form thermally stable molecules. In all molecules tested so far by the authors with decomposition points above 820° F., all the atoms of the structural skeleton have been a part of the hybridized structure. Resonance stabilization, therefore, appears to be an essential structural feature for molecules of high thermal stability.

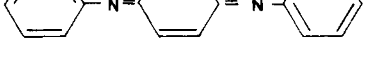
Bond strength and resonance interaction, however, are seldom limiting factors in the thermal stability of organic compounds, because most molecules decompose with activation energies lower than the bond energies of their weakest bonds. These molecules can decompose via a readily attainable transition state in which bonds are broken and formed simultaneously. Blocking the low-energy decomposition mechanism of a molecule should increase its activation energy and decomposition point.

A good example is the pyrolytic decomposition of esters. None of the bond energies in an ester are significantly weaker than those in a paraffin, yet bis(2-ethylhexyl) sebacate has a decomposition point of 543° F., while octacosane has a decomposition point of 662° F. The ester is believed to decompose via the following transition state, a quasi six-membered ring (*2*) which is very favorable sterically.



The activation energy for this reaction of 53.1 kcal. (compound 13) which is mush less than the 83 kcal. required for direct fission of a C—O bond. When this low-energy path was blocked by replacing the beta-hydrogen atoms of the alcohol moiety with alkyl groups, as in bis(1-methylcyclohexylmethyl) sebacate, the decomposition point was raised by 80° to 623° F., approaching that of octacosane, and the activation energy was increased to 57.8 kcal.

A second example of the increase in thermal stability resulting from blocking a low-energy decomposition path was given by the three phenylenediamines (compounds 63, 64, and 65). *N,N′*-Diphenyl-*p*-phenylenediamine is a molecule made up of strong bonds, all of which are resonance hybridized. It has, however, a low decomposition point, 509° F., because it can eliminate hydrogen to form the stable *N,N′*-diphenylquinonediimine,



Blocking this path by replacing the hydrogen atoms by methyl groups in *N,N'*-diphenyl-*N,N'*-dimethyl-*p*-phenylenediamine raised the decomposition point by 111° to 620° F. Replacing the N—CH_3 bond by the more stable N—C_6H_5 bond raised the decomposition point an additional 236° to 856° F., the stability level of aromatic ethers and aromatic hydrocarbons. In this case thermal stability was increased by 347° F. by blocking a low-energy path.

Although a molecule has available no simple, low-energy intramolecular decomposition path, its thermal stability and energy of activation of decomposition may still be less than expected from the strength of its bonds. In octacosane, the C—C bond energy is 82.6 kcal. and the C—H 98.7 kcal. The energy of activation as approximated by E', however, is not 82.6 kcal., but about 58 kcal. The free radical chain decomposition of hydrocarbons proposed by Rice (*10*) seems to account for this lower activation energy

$$R\cdot + R'\text{-}CH_2CH_2R'' \rightarrow R\text{-}H + R'\text{-}CH\text{-}CH_2R''$$

$$R'\text{-}CH\text{-}CH_2\text{-}R'' \rightarrow R'CH{=}CH_2 + R\cdot''$$

Although the radicals, R·, are formed initially by dissociation of a bond, subsequent steps in the chain reaction, transfer and decomposition of radicals, are low-energy processes so that the activation energy of the over-all reaction is lower than the energy of the bond broken to initiate the chain. This reaction path cannot be blocked by simple structural modification, but might be stopped by free radical inhibitors.

In the thermal breakdown of compounds, such as esters, which can decompose intramolecularly, the free radical chain decomposition may to some degree occur simultaneously. The higher the activation energy of the intramolecular transition state, the greater will be the participation of the chain mechanism in decomposition. The difficulty of inhibiting free radical decomposition of aliphatic compounds imposes an upper thermal stability limit of about 660° F. for any molecule containing a long alkyl group. No exception to this generalization has been found.

Thus, the most stable aliphatic compounds—with the possible exception of the cycloaliphatics—were shown to be normal paraffins. A few groups such as silane, silicate, or borate can be introduced into a paraffin chain without reducing thermal stability. Most structural modifications of normal paraffins, however, such as branching or introduction into the chain of groups such as ether, ester, amide, or phosphate lower the stability by 40° to 280° F. either by inducing more favorable sites for free radical attack or by opening paths for low-energy decomposition mechanisms.

Although it has not been demonstrated in this work, it appears reasonable that multiple linking may be significant in the thermal stability of complex aromatic molecules such as phthalocyanines, inorganic compounds, and possibly bicyclic aliphatics. In such molecules, bond rupture does not result in decomposition; rather the atoms are held together as if in a cage which allows the bond-breaking energy to be redistributed among the multiple bonds and the ruptured bonds to heal. The extreme thermal stability of many inorganic solids may be related to this factor, rather than to unusually high bond strengths.

An analogous "cage effect" has been invoked by Porter and Strachan (*13*) to explain their observation that on photolysis, in the glassy state, benzyl radicals are formed more readily from toluene ($C_6H_5CH_2$—H, 77.5 kcal.) than from ethylbenzene ($C_6H_5CH_2$—CH_3, 63 kcal.). The C—H bond underwent more decomposition than the weaker C—C bond, because it was easier for the resulting hydrogen atom to diffuse away from the benzyl radical than for the larger methyl radical to do so. Although ethylbenzene may be presumed to have momentarily dissociated, the radicals were effectively enclosed in a cage formed by the surrounding molecules, and thus readily recombined.

The principles discussed and the data presented in this article should give an insight into the factors which are important in the thermal degradation of organic compounds. More important, they should point the way for the tailoring of a molecule, with optimum thermal stability, for a given use.

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