THE INFLUENCE OF CHEMICAL STRUCTURE AND COMBUSTION REACTIONS ON THE MAXIMUM EXPERIMENTAL SAFE GAP OF INDUSTRIAL GASES AND LIQUIDS

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Summary

The paper shows how the molecular structure of a compound and the nature of the intermediates formed during its combustion can influence the Maximum Experimental Safe Gaps (MESGs). A qualitative discussion estimates the MESG of compounds for which measurements are not available by comparing their molecular structure and combustion products with those of compounds having measured MESGs. A list of compounds is given with measured MESGs corrected to standard temperature and pressure. The MESGs of compounds in various species groups are positioned on figures to show how molecular structure affects the MESG.

Introduction

The Maximum Experimental Safe Gap (MESG) of a gas or vapour that forms a flammable atmosphere with air is defined as the maximum normal distance between parallel surfaces that will prevent the explosion of any gas—air or vapour—air mixture on one side of the gap from igniting any mixture of the same gases on the other side. The MESG is important for the design of flameproof enclosures for electrical equipment used in flammable atmospheres.

The Physikatisch-Technische Bundesanstalt (PTB) has published MESGs for a range of gases and vapours [1]. A new apparatus similar to the PTB apparatus and in all essential respects identical, has been used to measure MESGs quickly at elevated temperatures and the MESGs of 63 gases and vapours have been tested [2]. The MESGs from both lists have been corrected to standard temperature and pressure (20°C and 100 kPa) using a procedure given elsewhere [2], and combined to give values for 110 gases and vapours (see Table 1). The MESGs of some compounds have been measured by both apparatuses and agreement is close.

If no measured value of the MESG is available for a compound, it would be useful to be able to estimate the likely value of the MESG by comparison with measured values for related compounds and hence the grouping of the

TABLE 1

Experimental values of the maximum experimental safe gap
(the compounds are listed under the heading of their organic type)

	Formula	MESG	Temp. (°C)	Corrected MESG (mm) (100 kPa, 20°C)	Group
1. Alkanes					
Methane	CH$_4$	1.14	20	1.14	IIA
Ethane	C—C	0.91	20	0.91	IIA
Propane	C—C—C	0.92	20	0.92	IIA
Butane	C—C—C—C	0.98	20	0.98	IIA
Pentane	C—C—C—C—C	0.93	20	0.93	IIA
	C				
Isopentane	C—C—C—C	0.96	20	0.96	IIA
Hexane	C—C—C—C—C—C	0.93	20	0.93	IIA
Heptane	C—C—C—C—C—C—C	0.91	20	0.91	IIA
Octane	C—C—C—C—C—C—C—C	0.94	20	0.94	IIA
	C				
Iso-octane	C—C—C—C—C—C	1.04	20	1.04	IIA
2. Alkenes					
Ethylene	C=C	0.65	20	0.65	IIB
Propene	C=C—C	0.94	20	0.94	IIA
1-Butene	C=C—C—C	0.94	20	0.94	IIA
2-Butene	C—C=C—C	0.89	20	0.89	IIB
1-Heptene	C=C—C—C—C—C—C	0.97	20	0.97	IIA
1,3-Butadiene	C=C—C=C	0.79	20	0.79	IIB
3. Alkynes					
Acetylene	C≡C	0.37	20	0.37	IIC
Propyne	C≡C—C	0.74	20	0.74	IIB

Compound	Structure				
4. Cyclic hydrocarbons					
Cyclopropane	C–C–C	0.91	20	0.91	IIA
Cyclopentane	C–C–C–C–C	1.01	20	1.01	IIA
5. Alcohols					
Methanol	C–OH	0.92	20	0.92	IIA
Ethanol	C–C–OH	0.89	20	0.89	IIB
1-Propanol	C–C–C–OH (C)	0.86	51	0.89	IIB
2-Propanol	C–C–OH	0.99	20	0.99	IIA
1-Butanol	C–C–C–C–OH	0.88	64	0.91	IIA
1-Heptanol	C–C–C–C–C–C–C–OH	0.88	100	0.94	IIA
1-Octanol	C–C–C–C–C–C–C–C–OH	0.95	116	1.03	IIA
Allyl alcohol	C=C–C–OH	0.84	30	0.84	IIB
6. Nitro-compounds					
Nitromethane	C–NO$_2$	1.11	87	1.17	IIA
Nitroethane	C–C–NO$_2$	0.84	67	0.87	IIB
1–Nitropropane	C–C–C–NO$_2$	0.81	71	0.84	IIB
Nitrobenzene	⬡–NO$_2$	0.86	127	0.94	IIA
7. Chloro-hydrocarbons					
Vinyl cloride	C–C–Cl	0.99	20	0.99	IIA
Allyl chloride	C=C–C–Cl (Cl)	1.17	20	1.17	IIA
1,1-Dichloroethylene	C=C–Cl	3.91	20	3.91	IIA
1,2-Dichloroethane	Cl–C–C–Cl	1.80	30	1.80	IIA
Butyl chloride	C–C–C–C–Cl	1.06	20	1.06	IIA
8. Amines					
Propylamine	C–C–C–NH$_2$	1.13	20	1.13	IIA
Butylamine	C–C–C–C–NH$_2$	1.16	20	1.16	IIA
1,2-Ethanediamine	NH$_2$–C–C–NH$_2$	1.47	61	1.55	IIA

TABLE 1 (continued)

Formula	MESG	Temp. (°C)	Corrected MESG (mm) (100 kPa, 20°C)	Group

9. Nitriles

	Formula	MESG	Temp. (°C)	Corrected MESG (mm)	Group
Hydrogen cyanide	H—CN	0.80	20	0.80	IIB
Acetonitrile	C—CN	1.50	20	1.50	IIA
Acrylonitrile	C=C—CN	0.87	20	0.87	IIB
10. Thiols					
Ethanethiol	C—C—SH	0.90	30	0.90	IIA
11. Aldehydes					
Formaldehyde	$H_2C{=}O$	0.57	20	0.57	IIB
Acetaldehyde	C—C—H ($=O$)	0.92	20	0.92	IIA
Propionaldehyde	C—C—C—H ($=O$)	0.84	20	0.84	IIB
Butyraldehyde	C—C—C—C—H ($=O$)	0.92	20	0.92	IIA
Crotonaldehyde, (E)	C—C=C—C—H	0.81	20	0.81	IIB
12. Ketones					
Acetone	C—C—C ($=O$)	1.04	20	1.04	IIA
2-Butanone	C—C—C—C ($=O$)	0.92	20	0.92	IIA

Compound	Structure				Group
2-Pentanone	C—C—C—C—C (O=)	0.99	30	0.99	IIA
3-Pentanone	C—C—C—C—C (O=)	0.88	48	0.90	IIA
Methyl isobutyl ketone	C—C—C—C (O=, O=)	0.98	60	1.01	IIA
2,4-Pentanedione	C—C—C—C—C	0.95	70	0.99	IIA
Cyclohexanone	C—C—C—C—C—C=O	0.95	60	0.98	IIA
13. Carboxylic acids					
Formic Acid	HC—OH (O=)	1.76	85	1.86	IIA
Acetic Acid	C—C—OH (O=)	1.69	73	1.76	IIA
14. Ethers					
Dimethyl ether	C—O—C	0.84	20	0.84	IIB
Diethyl ether	C—C—O—C—C	0.87	20	0.87	IIB
Di-isopropyl ether	C—C—C—O—C—C—C (C, C)	0.86	45	0.88	IIB
Dibutyl ether	C—C—C—O—C—C	0.94	20	0.94	IIA
2-Methoxyethanol	C—O—C—C—OH	0.81	63	0.84	IIB
2-Ethoxyethanol	C—C—O—C—C—OH	0.78	78	0.84	IIB
Ethanol, 2-(2-ethoxyethoxy)	C—C—C—O—C—C—O—C—C—OH	0.86	120	0.94	IIA
Ethanol,2-(2-butoxyethoxy)	C—C—C—C—O—C—C—O—C—C—OH	1.01	130	1.11	IIA
Chlormethoxymethane	C—O—C—Cl	1.00	20	1.00	IIA

TABLE 1 (continued)

Formula	MESG	Temp. (°C)	Corrected MESG (mm) (100 kPa, 20°C)	Group
15. Esters				
Formic acid, methyl ester	0.94	20	0.94	IIA
Formic acid, ethyl ester	0.94	20	0.94	IIA
Acetic acid, ethyl ester	0.99	20	0.99	IIA
Acetic acid, vinyl ester	0.94	20	0.94	IIA
Acrylic acid, methyl ester	0.86	20	0.85	IIA
Acrylic acid, ethyl ester	0.86	20	0.86	IIA
Methacrylic acid, methyl ester	0.99	30	0.99	IIA
Methacrylic acid, ethyl ester	1.01	30	1.01	IIA
Acetoacetic acid, methyl ester	0.96	101	1.03	IIA
Acetoacetic acid, ethyl ester	0.98	103	104.	IIA
Ethanol, 2-ethoxy-, acetate	0.91	73	0.95	IIA
Oxalic acid, diethyl ester	0.90	112	0.97	IIA

16. Anhydrides

	Structure				
Acetic anhydride	C—C—O—C—C (O=, =O)	1.17	78	1.23	IIA

17. Amides

	Structure				
N,N-Dimethyl formamide	C—N—C—O (C=, =N)	1.02	90	1.08	IIA

18. Cyclic ethers

	Structure				
Ethylene oxide	⌐C—C—O⌐	0.59	20	0.59	IIB
Propylene oxide	⌐C—C—C—O⌐	0.70	20	0.70	IIB
Dioxan	⌐O—C—C—O—C—C⌐	0.70	20	0.70	IIB
Furan	⌐O—C=C—C=C⌐	0.68	20	0.68	IIB

Ethers

	Structure				
Tetrahydrofuran	⌐O—C—C—C—C⌐	0.87	20	0.87	IIB
Tetrahydrofurfuryl alcohol	⌐O—C—C—C—C⌐—C—OH (=O)	0.80	100	0.85	IIB
2-Furfuraldehyde	⌐O—C—C=C—C⌐—H	0.88	94	0.94	IIA
1,3,5-Trioxalene	⌐O—C—O—C—O—C⌐	0.71	90	0.75	IIB
Morpholine	⌐O—C—C—NH—C—C⌐	0.92	58	0.95	IIA
Propane, 1-chloro-2,3-epoxy	⌐O—C—C—C⌐—Cl	0.95	58	1.00	IIA

19. Thiophenes

	Structure				
Thiophene	S—C=C—C=C	0.92	20	0.92	IIA
Tetrahydrothiophene	S—C—C—C—C	0.99	20	0.99	IIA

TABLE 1 (continued)

	Formula	MESG	Temp. (°C)	Corrected MESG (mm) (1000 kPa, 20°C)	Group
20. Aromatic compounds					
Benzotrifluoride	⬡—CF$_3$	1.40	20	1.40	IIA
Butyl styrene	⬡—C—C—C—C / —C	0.99	20	0.99	IIA
21. Miscellaneous					
Hydrogen	H$_2$	0.29	20	0.29	IIC
Carbon monoxide (moist)	CO	0.94	20	0.94	IIA
Carbon disulphide	CS$_2$	0.34	20	0.34	IIC
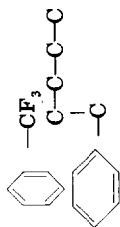
compound. The groupings are laid down by the International Electro-
technical Commission (IEC) [3] and are as follows:

Group I	—	firedamp only
Group IIA	—	MESG $\geqslant$ 0.9 mm
Group IIB	—	0.9 > MESG $\geqslant$ 0.5 mm
Group IIC	—	MESG < 0.5 mm

Attempts have been made to generalise the effects of molecular structure
on combustion parameters [4], but Salooja [5] has demonstrated that it is
not the resistance of the basic structure of hydrocarbon fuels to chemical
attack, but the combustion processes that determine the pre-flame and igni-
tion behaviour, and hence the susceptibility of a hydrocarbon fuel to self-
ignition. This paper estimates the MESGs of compounds based on the nature
of the intermediate species formed in the combustion processes.

Hot jet ignition

Phillips [6] developed a theory to explain the behaviour of safe gaps. A
hot jet of gases is cooled when the jet entrains cold, unburned gas from the
external mixture. The MESG of a compound is found when the rate of
heating by burning is balanced by the rate of cooling by entrainment. The
rate of burning depends on the chemical reaction rate and the rate of
entrainment depends on the jet velocity.

Bray and Fletcher [7] have suggested that the length of the potential core
of the hot jet also determines whether or not the hot jet will ignite the ex-
ternal cold mixture. As the hot jet entrains the cold mixture, the rate of fall
in temperature beyond the tip of the potential core causes rapid quenching
of the highly temperature-dependent reactions and, if a critical point in the
ignition reaction has not been reached before this quenching occurs, ignition
will not take place. Fluid mixing time takes account of both the jet velocity
and potential core length and is defined as the time taken by a fluid particle
to travel the length of the potential core at the initial velocity of the jet.
Chemical reaction rate can be expressed in terms of ignition time, which
depends on the reaction mechanisms. The ignition reaction occurs in the
region of rapid intermixing of hot and cold fluids and the rate of reaction
which leads to ignition is controlled by chemical kinetics. So, the MESG can
be defined in terms of ignition time and fluid mixing time.

During an MESG measurement, as the flange gap is widened, the length
of the potential core of the hot jet increases and so the fluid mixing time in-
creases and eventually exceeds the ignition time. The gap width at which the
ignition time and the fluid mixing time are equal defines the MESG.

Vanpee and Wolfhard [8], Kuchta and Cato [9] and Wolfhard and
Vanpee [10] have done experiments on the effects of changes in initial jet
temperature, initial jet velocity and jet diameter on the ignition behaviour of
hot inert laminar jets which show, qualitatively, that the theory of a critical
point in the ignition process is plausible. The experiments also showed that,

although the ignition time of a flammable fuel—air mixture is dependent on the fuel concentration, changes in the fuel concentration in the external cold flammable mixture have little effect on the ignition behaviour of hot laminar jets. Extending, to other organic compounds, Salooja's suggestion [5] that the relative susceptibility to ignition of hydrocarbons is determined by the combustion reactions occurring in the pre-ignition dalay rather than by resistance of the original fuel to chemical attack, then the ignition time will depend on the species formed in the combustion processes and the reactions they undergo.

Structure effects on MESG

In the following qualitative discussion, the relationship between chemical structure of compounds and their measured MESGs, corrected to 20°C and 100 kPa, is discussed. Secondary effects such as fuel concentration in the flammable mixture are discounted. The discussion centres on the major intermediate species produced by combustion of the compound. The discussion is brief and does not attempt a complete analysis of reaction mechanisms, but outlines the typical species which occur in combustion reactions and shows how comparisons of reactions and intermediates can give an estimate of MESG for compounds that have not been tested but have some similarity to those compounds for which measurements are available.

Some of the measured MESGs from Table 1 are shown graphically in Figures 1—5. The graphs are designed to show the effects of molecular structure on MESGs.

Hydrocarbons
The MESGs of a range of hydrocarbons are shown in Fig. 1.

Alkanes: saturated hydrocarbons
All the alkanes can be grouped as IIA compounds. Salooja [11] found that above 500°C the ignition behaviour of hydrocarbons reflects the nature and strength of the bonds in a molecule, and shock ignition studies of n-heptane [12] and other linear alkanes have revealed substantial pre-flame cracking. The high value of the MESG of methane compared with the MESGs of other alkanes is a result of a much slower rate of initial decomposition, requiring the breaking of a C—H bond. (The decomposition of higher alkanes involves the breaking of the weaker C—C bond). Slower decomposition leaves a large fraction of the initial methane unreacted by the end of the pre-ignition period, whereas a large fraction of ethane, for instance, has disappeared by the end of its pre-ignition period. The slow decomposition of methane extends the whole of the ignition time, resulting in a high MESG.

The rates of initial decomposition and the reaction mechanisms are similar as the series of higher alkanes is ascended. The intermediate species include alkyl radical products, the alkene corresponding to the original alkane and
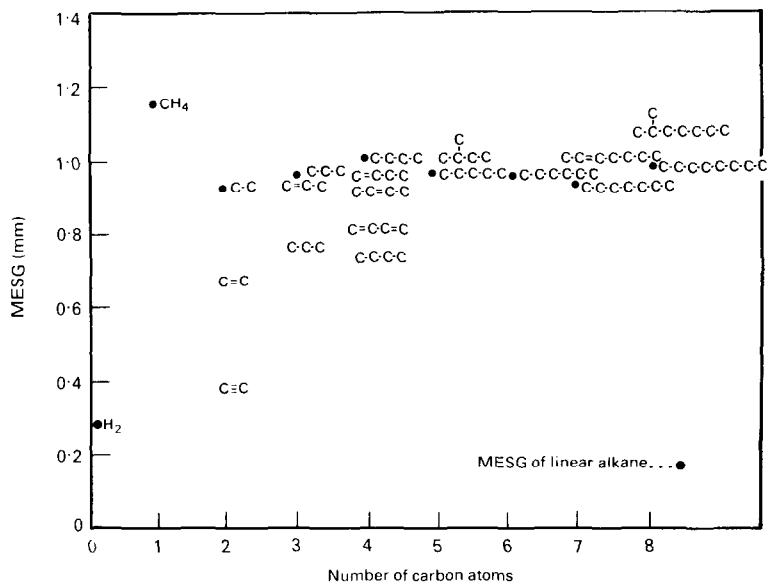
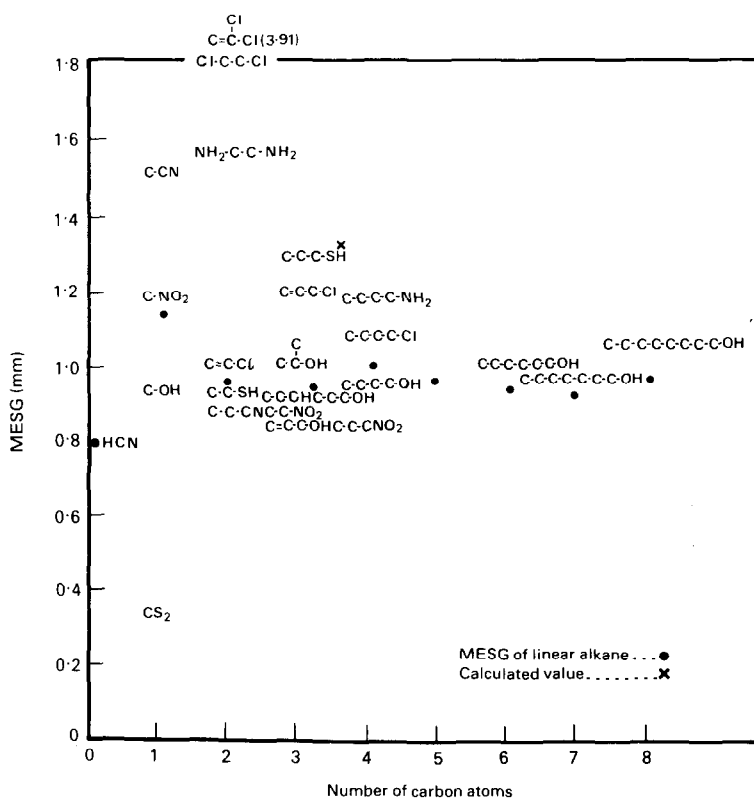Fig. 1. Effect of molecular structure on the MESG of hydrocarbons.

Fig. 2. Effect of molecular structure on the MESG of substituted hydrocarbons.
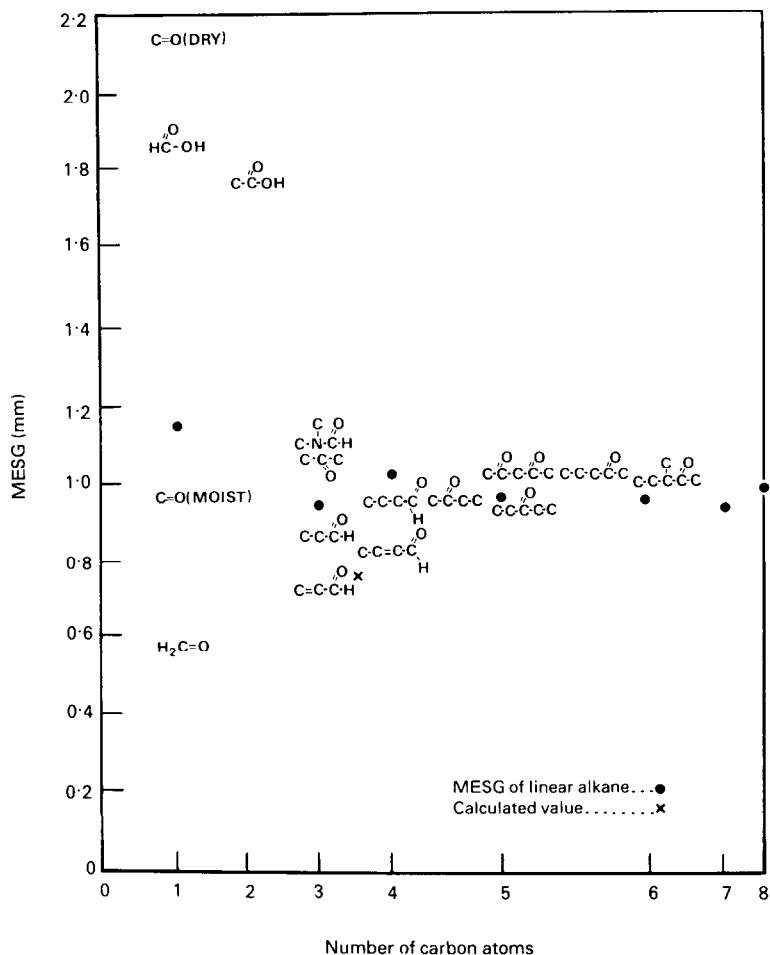
Fig. 3. Effect of molecular structure on the MESG of aldehydes, ketones and carboxylic acids.

allyl radical (or similar) products of the alkene reactions. Satterfield and Reid [13] found that allyl radicals are slow to react in oxidation mechanisms; hence they extend the ignition time, increasing the MESG. The similar mechanisms and rate during the pre-ignition periods leads to almost equal MESGs for the higher alkanes.

Alkenes and alkynes: unsaturated hydrocarbons

The same intermediates and similar mechanisms occur in the combustion of an alkene as occur in the combustion of the corresponding alkane: the measured MESGs reflect this similarity. For example, propane and propene both produce allyl radical intermediates which inhibit the reaction rate and result in the measured MESGs of the two fuels being equal, within experi-

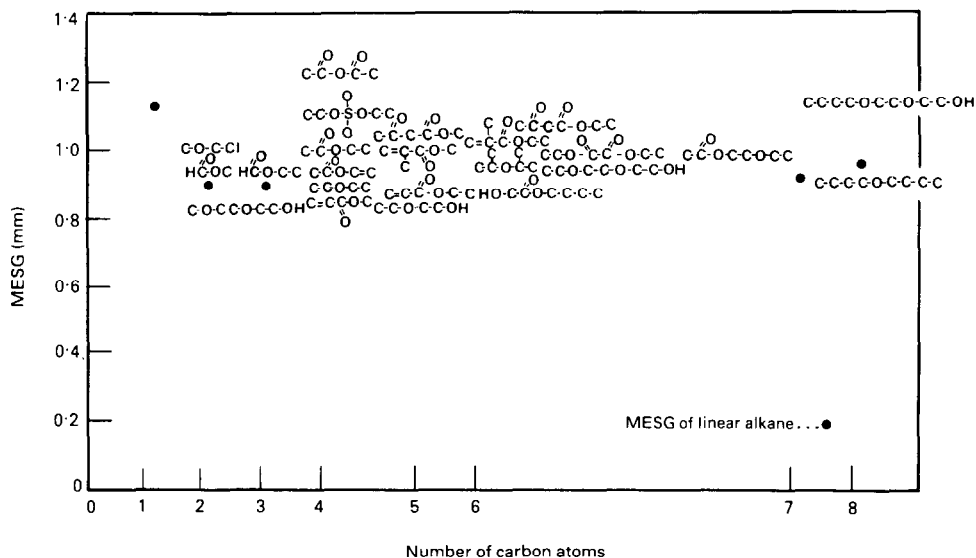Fig. 4. Effect of molecular structure on the MESGs of ethers, esters and anhydrides.
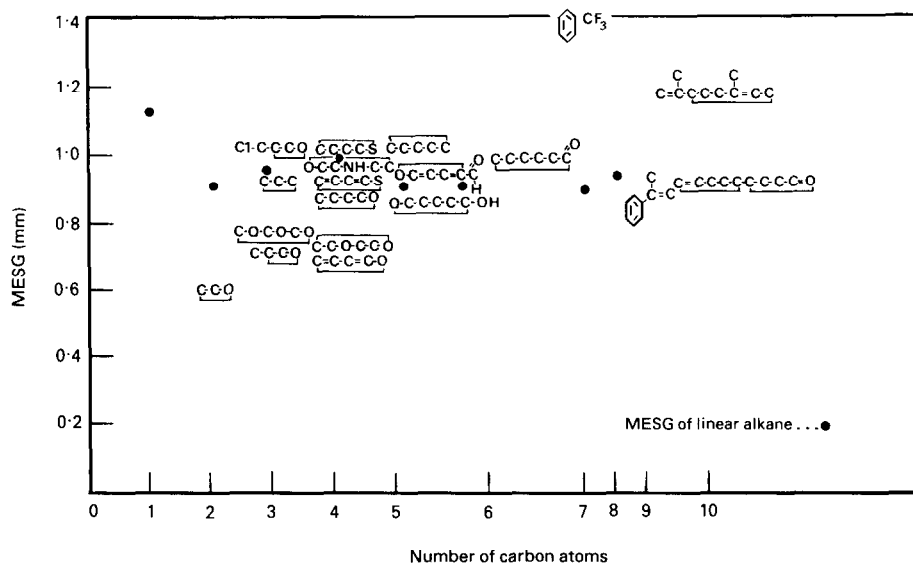

Fig. 5. Effect of molecular structure on the MESG of cyclic compounds.

mental error. All linear mono-alkenes, except 2-butene and ethylene, can be grouped with the alkanes as IIA compounds.

The combustion reactions of 2-butene and ethylene produce the vinyl radical, $CH_2 = CH$, which in turn produces acetylene. The vinyl radical is

only produced during the initial decomposition of 2-butene but is produced extensively throughout the whole pre-ignition period of ethylene. The influence of the vinyl radical production in the ignition reactions is reflected in the values of the measured MESGs; ethylene has a lower MESG than 2-butene. Alkenes that can, at some period in the pre-ignition reaction, produce vinyl radicals can be grouped as IIB compounds; for example, butadiene. The chemical structures of compounds such as isobutene and trimethyl ethylene suggest that they be included in Group IIB, although their combustion reactions produce less active C_3 species in place of vinyl radicals or acetylene.

Acetylene is the most reactive hydrocarbon, has the lowest MESG and is grouped as a IIC compound. In comparison with the measured MESGs of propyne and butyne, higher mono-alkynes should be classed as Group IIB.
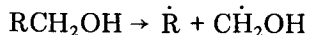
Unsaturated hydrocarbons containing more than one unsaturated carbon—carbon bond can, if those bonds are well separated, be grouped by reference to the bond with the greatest degree of unsaturation. Compounds in which a triple and double bond are close together, e.g. $C{\equiv}C{-}C = C$, are highly reactive and should be grouped in IIC.
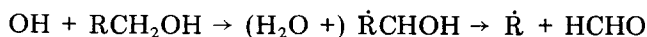
Substituted hydrocarbons

The MESGs of a range of substituted hydrocarbons are shown in Fig. 2.
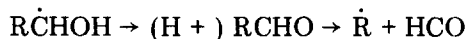
Alcohols: substitution by OH

The combustion of linear saturated alcohols produces, as an important intermediate, the alkyl radical containing one less carbon atom than the original alcohol. The radical is a product of the initial decomposition

$$RCH_2OH \rightarrow \dot{R} + \dot{C}H_2OH$$

and of later reactions such as

$$OH + RCH_2OH \rightarrow (H_2O +) \dot{R}CHOH \rightarrow \dot{R} + HCHO$$

and

$$R\dot{C}HOH \rightarrow (H +) RCHO \rightarrow \dot{R} + HCO$$

The combustion intermediates of the alkane corresponding to this alkyl radical and of the original alcohol are the same. Propanol and higher alcohols have MESGs that are approximately equal to the MESGs of the alkane with one less carbon atom. For example, the MESGs of butanol and propane are equal, within experimental error, and reflect the presence of propyl and allyl radicals, and of propene in the pre-ignition reactions.

Methanol and ethanol both yield methyl radicals as important combustion intermediates, but have different MESGs from methane, which is exceptional because of its slow rate of decomposition. The intermediate methyl radicals play an important part in the ignition delay of small compounds leading to almost equal values of MESG for methanol, ethanol, ethane and acetalde-

hyde. All the linear saturated alcohols have MESG values similar to those of the alkanes above methane, i.e. around the 0.9 mm group boundary. Ethanol and propanol have the lowest MESGs of the linear saturated alcohols and are classed as Group IIB; the other compounds are classed as Group IIA.

This explanation can be extended to unsaturated alcohols: alcohols that produce allyl-type radicals as combustion intermediates can be safely classed in Group IIA. Alcohols yielding vinyl-type radicals are classed in Group IIB, e.g. allyl alcohol. The grouping of non-linear alcohols should be based upon the structure of the typical radical produced by combustion and the grouping of its corresponding hydrocarbon.

Nitro compounds — substitution by —NO_2
Three linear nitroalkane MESGs have been measured and, by comparison with the MESG of the corresponding alcohol, indicate that substitution of the —NO_2 group in place of the ·OH group generally increases the reactivity, i.e. the MESG is decreased. Only in the case of nitromethane does the —NO_2 group appear to act as an inhibitor, probably because the initial decomposition requires the breaking of a stronger C—N bond rather than the weaker C—C bond of the higher nitroalkanes. All nitroalkanes apart from nitromethane can be classed as Group IIB compounds, nitromethane is classed as Group IIA.

Chlorinated hydrocarbons — substitution by—Cl
Rosser and others [14] found that substituion of chlorine atoms into a hydrocarbon inhibits ignition, and the extent of inhibition can be correlated with the chlorine content of the molecule. During a pre-ignition period, inhibition is a function of the rate of release of chlorine atoms from the molecule. The dissociation energies of the C—Cl bonds in mono-chloro compounds are in the order vinyl chloride > butyl chloride > allyl chloride and this order is reflected in the relative values of the MESGs (vinyl chloride < butyl chloride < allyl chloride).

All chloroalkanes and chloroalkenes can be classed in Group IIA.

Amines: substitution by —NH_2
Substitution by —NH_2 acts inhibitively on the ignition of the unsubstituted hydrocarbon. Cullis and others [15] give the order of ignition inhibition of n-heptane as dimethylamine > monomethylamine > trimethylamine, and this order is reflected in the MESGs of these amines as measured in an 8-litre apparatus by Sack and Soeder [16].
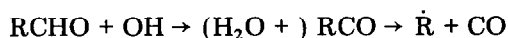
Carbonyl compounds
The MESGs of a range of aldehydes, ketones and carboxylic acids are shown in Fig. 3.

Aldehydes

Aldehyde combustion mechanisms involve the reactions

$$RCHO \rightarrow \dot{R} + HCO$$

and

$$RCHO + OH \rightarrow (H_2O +) RCO \rightarrow \dot{R} + CO$$
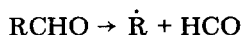
As with alcohols, linear aldehydes are comparable with the hydrocarbon containing one less carbon atom.

Butyraldehyde has an MESG equal to those of butanol, propane and propene within experimental error; propionaldehyde has an MESG approximately the same as that of propanol and ethane; acetaldehyde has an MESG close to the values of other small compounds that produce methyl radicals during combustion. Formaldehyde is a highly reactive compound; its combustion involves more reactive H atoms in place of alkyl radicals. Formaldehyde is clearly a Group IIB compound, but of the higher aldehydes with a saturated carbon chain only propionaldehyde falls into Group IIB; all others can be classed as Group IIA. The slightly lower MESGs of propionaldehyde and propanol in their series reflect the presence of ethyl radical intermediates in the combustion mechanisms which slightly increase the pre-ignition reaction rate. Unsaturated aldehydes that produce allyl-type radical intermediates during combustion can be classed as Group IIA and those that produce vinyl-type radical intermediates can be classed as Group IIB.

Ketones

The substitution of a hydrocarbon group in place of the aldehyde H converts an aldehyde into a ketone and invariably increases the MESG by replacing the H radical in the combustion mechanism by a less reactive intermediate. This effect is noticeable in the MESG values of methyl ketones: the MESG is increased compared to that of the corresponding aldehyde, but increases or decreases in the MESG, occurring as the carbon chain of the ketone lengthens, correspond to the changes that occur as the aldehyde series is ascended.

All ketones with saturated carbon chains can be classed as Group IIA, except 3-pentanone, which falls into Group IIB. 3-Pentanone (diethyl ketone) has a molecule with two sources of ethyl radicals, which slightly increase the pre-ignition reaction rate.

Unsaturated ketones that produce vinyl-type radical intermediates during combustion can be classed as Group IIB, those that produce allyl-type radicals can be classed as Group IIA.
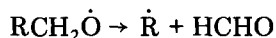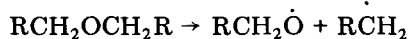
Carboxylic acids

Replacement of the aldehydic-H by an OH group converts an aldehyde into a carboxylic acid. These acids are unreactive and produce large amounts of CO_2 during combustion. They can be classed as Group IIA compounds.
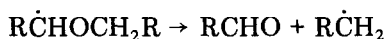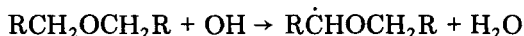
Other oxygenated compounds

The MESGs of a range of ethers are given in Fig. 4.

Ethers

Ether combustion mechanisms involve the initial reactions

$$RCH_2OCH_2R \rightarrow RCH_2\dot{O} + \dot{R}CH_2$$

$$RCH_2\dot{O} \rightarrow \dot{R} + HCHO$$

and subsequently

$$RCH_2OCH_2R + OH \rightarrow R\dot{C}HOCH_2R + H_2O$$

$$R\dot{C}HOCH_2R \rightarrow RCHO + R\dot{C}H_2$$

The formaldehyde produced in the early stages of the reaction is a reactive intermediate that causes slight deceases of the MESGs compared with the MESGs of other compounds that produce the same hydrocarbon radical as a combustion intermediate. All linear ethers can be classed as Group IIB compounds. The combustion of di-isopropyl ether produces acetaldehyde in the place of formaldehyde and decreased reactivity results in a high MESG and puts the compound in Group IIA. Other saturated ethers that do not produce formaldehyde can also be classed as Group IIA. Unsaturated ethers can be classed according to the hydrocarbon radical combustion intermediates. Linear unsaturated ethers will be IIB compounds.

Compounds such as 2-methoxyethanol and 2-ethoxyethanol can be grouped in the same ways as ethers as their combustion reactions are similar to those of the ethers.

Esters

The combustion intermediates of esters are hydrocarbon radicals formed by splitting off both the acid carbon chain and the alcohol carbon chain. The combustion reactions of the hydrocarbon radicals determine the MESGs of the esters. Experimental measurement shows that for formic acid, acrylic acid, methacrylic acid and acetoacetic acid, the methyl and ethyl esters have equal MESGs within experimental error. The difference in measured MESGs between, say, the acrylates and methacrylates is caused by the reactivity of the different hydrocarbon radicals produced from the different acid chains. Generally, esters with saturated alcohol chains can be grouped by reference to the MESG of the methyl and ethyl esters. The great majority of such esters will be classed in Group IIA, although, it must be noted, the acrylates are classed in Group IIB.

Similarly, the presence of a double bond in the alcohol chain may reduce the MESG. Acetic acid, vinylester has a lower MESG than the ethyl ester acetate. Generally, if splitting off the alcohol chain produces a vinyl-type hydrocarbon radical, the MESG will be lower than that of the comparable saturated ester.

Cyclic compounds

The MESGs of a range of cyclic compounds are shown in Fig. 5. In some cases cyclic compounds have MESGs similar to those of their linear counterparts. Cyclopropane is isomerized to propene during combustion and the MESGs of these compounds are equal. Other compounds with MESGs similar to their linear counterparts include cycloalkanes, cyclic aldehydes and cyclic ketones and large saturated cyclic monoethers and diethers.

Small cyclic monoethers and large, unsaturated cyclic ethers have low MESGs. For instance, formaldehyde is an important combustion intermediate of ethylene oxide, and the MESGs of these two compounds are equal.

Conclusion

An analysis of the MESGs of compounds with a wide range of molecular structures shows that variations in the value of MESG can be related to chemical structure and the mechanism of combustion. The relationship depends largely on the nature of the intermediate species formed during combustion.

If the MESG of a compound has not been measured, a useful estimate of its probable value, and hence of the grouping of the compound, can be made by comparing the molecular structure and likely combustion intermediates with those of compounds having known values of MESG.

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