Thermal Stability of Some Organic Compounds

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Descriptions of four types of test apparatus, the definition of the decomposition point, observations on the effect of pressure on rate of decomposition, discussion of thermal stability as related to chemical structure, and statement of conclusions appeared in *I&EC Product Research and Development (Quarterly)*, March 1962.

AN EXTENSIVE study of the thermal stability of various types of organic compounds has been made, to determine those types that should be most useful for the synthesis of stable fluids. The data obtained are presented here, together with some correlations between thermal stability and chemical structure.

The methods are designated by *V*, *G*, *H*, and *D*. The first or vapor phase method gives the temperatures at which decomposition can be detected by evolution of gas. The other three methods employ the sample in the liquid or solid state. For them, the decomposition point is that temperature at which the compound decomposes at the rate of 1 mole % per hour.

MATERIALS

The samples tested were obtained commercially when available or were prepared using methods in the literature. They were all purified by distillation, recrystallization, and/or sublimation, as applicable. The following compounds were prepared by new syntheses.

Diphenyldicyanomethane. This was prepared by heating 56 grams of diphenyldichloromethane with 50 grams of cuprous cyanide to about 100° C. for 3 hours after the initial reaction subsided, and the product was extracted from the residue with hot benzene or petroleum ether and purified by digesting with Norit and recrystallizing. The product melted at 88-9° C. The yield was low and might be improved by use of an inert solvent to control the exothermic reaction. Analysis, calculated for $C_{15}H_{10}N_2$: C, 82.6; H, 4.6; N, 12.85. Found: C, 83.0; H, 4.8; N, 12.4.

Tri–2-pyridyl–*s*-triazine. The preparation was by quantitative high pressure condensation of 2-cyanopyridine without solvent at 200-275° C. and 6700 kg./sq. cm. The product after recrystallization from 50% ethyl alcohol and sublimation in a vacuum melted at 246° C. Case and Koft (*3*) prepared the same compound by heating the nitrile with sodium hydride. Yield was 56%, m.p. 244-5° C. for the trihydrate, which undoubtedly dehydrated before melting.

Hexaphenylphosphorazole. Phenyldichlorophosphine (53.7 grams, 0.3 mole) was added to a solution of 27.9 grams (0.3 mole) of aniline and 65 grams (0.65 mole) of triethylamine in 600 ml. of dry benzene under nitrogen while stirring and cooling. After addition (1 hour) the reaction mixture was refluxed 5 hours. After removal of triethylamine hydrochloride by filtration, a yellow solid in about 45% yield was isolated upon concentration of the benzene filtrate. A low-melting resinous solid of low molecular weight, probably a linear condensation product that is extremely soluble in benzene, was also isolated. The cyclic compound, the high-melting (264-5° C.) yellow solid, was difficult to purify. A really pure sample was not obtained, probably because of continued rearrangement of the cyclic trimer into the tetramer and linear polymer. Analysis, calculated for $C_{36}H_{30}N_3P_3$: C, 72.35; H, 5.06; N, 7.03; P, 15.55; molecular weight 597.6. Found C, 69.63; H, 5.20; N, 7.16; P, 14.97; molecular weight 590 (f. p. depression of benzene).

1,5,9- and 1,2-6-Tripyridinobenzene. The Cohn modification of the Skraup synthesis (*4*) from 1,3,5,- and 1,2, 4-triaminobenzene, respectively, was used. The 1,5,9-isomer was purified by several recrystallizations from ethyl alcohol followed by sublimation at 150° C. (10^{-4} mm.). The 1,2,6-isomer, a new compound, melted at 234-5° C. after sublimation at 225° C. (10^{-4} mm.). Analysis, calculated for $C_{15}H_9N_3$: C, 77.90; H, 3.92; N, 18.17. Found: C, 78.08; H, 3.97; N, 18.39.

STABILITY DATA

Aromatic Compounds. Several polyaromatics were tested (Table I) and found less stable than the parent compound. The polyphenyls decrease in stability with increasing ring linkages, but the effect quickly levels off. *p*-Quaterphenyl is about as stable as the biphenyl-terphenyl eutectic, which is much less stable than biphenyl. 1,3,5-Triphenylbenzene is about as stable as *p*-quaterphenyl, which has the same number of ring linkages. The lower stability of hexaphenylbenzene might be caused by steric interference. Although biphenyl is slightly more stabilized by resonance than benzene, the greater stabilization of the polyphenyl radicals over the phenyl radical may contribute to the lower stability of the polyphenyls. Decafluorobiphenyl has been reported as stable as hexafluorobenzene (*12*). This suggests that the C—C bond joining the rings is very stable. The C—F bond is more stable than the C—H bond, and the radical is less readily formed.

2,2′-Binaphthalene is more stable than 1,1′-binaphthalene. This is an illustration of the importance of choosing compounds that do not have an easy route to decomposition. The geometry of 1,1′-binaphthalene allows the easy formation of perylene with elimination of the hydrogen atoms on the 8-position, a path for decomposition that is not available to 2,2′-binaphthalene.

Substituted Aromatic Compounds. The most stable substituted aromatics were the perfluorinated or perchlorinated compounds. Hexafluorobenzene was much more stable than benzene. The C—F bond in hexafluorobenzene may be as high as 145 kcal. (*7*). Hexachlorobenzene and decachlorobiphenyl were also very stable. However, partially halogenated benzenes do not have this exceptional stability. Chloro- and dichlorobenzenes are less stable than benzene (*5*).

The effect of inserting other groups between phenyl rings is pointed out in Table I. Diphenyl ether is exceptionally stable, but polyphenyl ethers are somewhat less stable. Diphenylmethane is relatively stable. Substitution of the alkyl hydrogens by the electronegative substituents cyano- or fluoro- lowers the stability because of easy formation of HX with hydrogen from the benzene rings. Bibenzyl has poor stability. Stilbene and diphenylacetylene are somewhat more stable, probably because of the difference in stability of the C—C bond and C=C and C≡C bonds. Diphenylmethane is much more stable than diphenyldifluoromethane, but bibenzyl is less stable than 1,2-diphenyltetrafluoroethane.

Triphenylamine is very stable. Secondary amines are less stable (*1*). Tri-2-pyridylamine was a little less stable than triphenylamine. Pyridyl substituted in place of phenyl on the triazine ring also lowered stability. The low stability

Table I. Stability of Certain Compounds in the Condensed Phase

Aromatic compd.	Apparatus	Decompn. Temp., ° C.
Naphthalene[a]	H	570
Biphenyl[a]	H	543
Triphenylene	H	527
2,2′-Binaphthalene	H	518
2-Phenylnaphthalene	H	507
Biphenyl-terphenyl eutectic[b,c]	H	493
1,3,5-Triphenylbenzene	G	499
p-Quaterphenyl	H	482–504
Hexaphenylbenzene	G	453
1,1′-Binaphthalene	H	452
Coronene	G	453
Substituted aromatic compds.		
Hexachlorobenzene	H	510–27
Decachlorobiphenyl	D	510–20
Diphenyl ether	H	538
Triphenylamine	H	502
Tri-2-pyridylamine	H	452
Ferrocene	H	454
Diphenylmethane	H	454
m-Bis(*m*-phenoxyphenoxy) benzene	H	468–82
Bis[*m*-(*m*-phenoxyphenoxy)phenyl] ether	H	474
Diphenyldicyanomethane	D	427–40
1,2-Diphenyltetrafluoroethane	D	427–40
Diphenylacetylene[d]	H	421
Stilbene	H	418
Bibenzyl	D	382
Diphenylcarbodiimide	G	370
Diphenyldifluoromethane	D	318
Heterocyclic compd.		
Dibenzothiophene	H	545
Dibenzofuran	H	518
Quinoline	H	510–35
1,2,6-Tripyridinobenzene	G	482
2,2′-Biquinoline	G	> 482
2,2′-Bipyridine	H	482
2,2′-Bithiophene	H	474
1-Phenylimidazole[e]	H	477

Heterocyclic compd.	Apparatus	Decompn. Temp., ° C.
6-Phenylquinoline	H	477–85
8-Phenylquinoline	H	466
2-Phenoxypyridine[f]	H	457
Phenazine	H	452–65
1,10-Phenanthroline	H	432
Isoquinoline	H	438–63
1,5,9-Tripyridobenzene	G	441
1,2,4,5-Tetraphenylimidazole	H	443
2,2′-Biimidazole	H	< 427
Pyridazine	H	316
s-Triazine compd.		
Triphenyl-*s*-triazine	G	467
Hexaphenylmelamine	G	454
Tri-2-pyridyl-*s*-triazine	G	348
Cyanuric tricyanide	G	< 238
Silicon compd.		
Diphenyldiphenoxysilane	H	470–90
Tetraphenyl silane	H	482
Phenyl silicate	H	468
Polyphenoxysiloxane	H	390–418
Bis(*o*-phenylenedioxy)silane	H	316–66
Boron compd.		
o-Phenylenephenylboronate	H	496–507
Bis-*o*-phenylenedipyroborate	H	454
Hexaphenylborazole	G	434
Tris-*o*-phenylenebisborate	H	396
2-Phenyl-3-benzodiazaborole	D	368
Triphenylboroxole	G	357
Dimethylphosphinoborine trimer	H	< 357
Triphenylboron[g]	H	316–66
Phosphorus compd.		
Triphenylphosphine oxide	H	454
Diphenylphosphinic nitride tetramer	G	432
Triphenylphosphine sulfide	G	~380
Hexaphenylphosphorazole	G	352
Tri-2-pyridylphosphine sulfide	G	< 308

[a] Critical temperatures. Naphthalene 480° C.; biphenyl 528° C. [b] Eutectic is 25% biphenyl, 55% *o*-terphenyl, 20% *m*-terphenyl. [c] Decomposition temperature same with 2% acridine added. [d] Polymerized during test. [e] Rearranged partially to 2-phenylimidazole. [f] Rearranged quantitatively to *N*-phenyl-2-pyridone before decomposing. [g] Tested under argon.

of diphenylcarbodiimide eliminates this group as a useful connecting linkage.

Ferrocene was relatively stable, reflecting its aromatic character. The product isolated was diferrocenyl, formed by loss of hydrogen. Diferrocenyl is unstable at the decomposition point of ferrocene.

Under all test conditions decomposition of compounds with long alkyl substituents is more extensive than that of methyl-substituted compounds. Methyl-substituted aromatics in the condensed phase are about as stable as diphenylmethane.

Toluene in the vapor phase test (Table II) was only slightly less stable than benzene. Other workers (*11, 13*) have found that alkylbenzenes on decomposition yield different products in low-pressure, high-temperature tests than in liquid phase tests. The ratio of hydrogen to alkyl fragments is higher in vapor phase tests, although the ratio varies with different compounds.

Heterocyclic Compounds. Some of the most stable organic compounds are in this group. The molecular configuration, the position of the heterocyclic atom(s), and the nature of substituents all affect the stability. Dibenzothiophene and dibenzofuran, extremely stable compounds, are approximately 100° C. more stable than fluorene (which is a little less stable than diphenylmethane, decomposition point 454° C.). Carbazole has also been reported very stable (*11*). Phenazine, which has an anthracene configuration that was found relatively unstable among the aromatics by Madison and Roberts (*11*), is less stable. Aniline was found as a decomposition product, indicating ring breakage. The fluorene ring system is significantly more stable than the anthracene ring system.

Comparison of heterocyclics to the corresponding aromatic structure indicates that in the condensed phase the aromatic structure is more stable: quinoline (510–535° C.) and naphthalene (570°); 2,2′-bipyridine (482°), 2,2′-bithiophene (474°), 2,2′-biimidazole (under 427°) and biphenyl (543°); triphenylene (527°) and the tripyridinobenzenes (482° and 441°). In the vapor phase the heterocyclic compounds were slightly more stable: quinoline (650°) and naphthalene (620–650°); pyridine (620–650°) and benzene (600°); 2,2′-bipyridine (610–650°) and biphenyl (510–540°). This difference in relative stability may be due to decomposition taking place by different mechanisms.

The position of the hetero-atom can affect stability. For example, quinoline is more stable than isoquinoline. The two tripyridinobenzenes show some difference in stability. Two adjacent nitrogen atoms in a ring decrease stability appreciably. Imidazole, 1,2,4-triazole, and pyridazine are all relatively unstable. Two nitrogens in the 1,3-position in six or five-membered rings on the other hand were very stable (pyrimidine and imidazole).

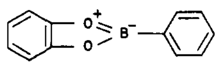
Substituents decreased stability as in the aromatics. The single exception was 2,2′-bipyridine, which was as stable as pyridine in the vapor phase only.

Benzothiazole and thiazole had comparable stability, but benzimidazole was much less stable than imidazole. The expected slight increase in stability from resonance stabilization could account for the slight increase in stability in benzothiazole over thiazole. Possibly greater resonance stability of the benzimidazole radical over that of the imidazole radical contributes to easier decomposition of the former compound.

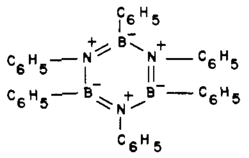
s-Triazines. The *sym*-triazines tested decomposed over a wide temperature range. The limit of stability is probably represented in triphenyl-*s*-triazine, except for very complex polymeric molecules containing triazine ring structures that would be more stable because of the "cage" effect. Replacing the phenyl group by the 2-pyridyl group lowered the stability significantly.

Silicon Compounds. The stability of compounds tested indicates that compounds made up of C_{phenyl}—O—Si and the C_{phenyl}—Si bonds have comparable stability. Polyphenoxysiloxane which has Si—O—Si linkages was less stable. The cyclic compound, bis(*o*-phenylenedioxy)-silane, was relatively unstable compared to a boron compound of similar structure, *o*-phenylenephenylboronate. The steric effect of the larger silicon atom may weaken the stability of the compound.

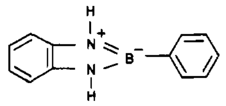
Boron Compounds. The cyclic compound *o*-phenylenephenylboronate was the most stable boron compound tested and among the most stable of all the compounds. The stability of this type compound has been noted before (*6, 9*) and attributed to 6 π electron resonance stabilization



The related compounds, tris-*o*-phenylenebisborate and the pyroborate, are not as stable. The resonance stabilization is apparently weaker in these compounds. Also, triphenylboroxole is relatively unstable. No compounds containing B—O—B were exceptionally stable. Hexaphenylborazole was more stable than the boroxole. This compound would be stabilized by resonance:



which is weaker with the more electronegative oxygen (*13*). Therefore, because of ring resonance stabilization, the stability of 2-phenyl-1,3-benzodiazaborole would be expected to be exceptional



unless the N—H bonds are a weak link. In fact, it is less stable than the boronate.

Dimethylphosphinoborine trimer, which is a coordination compound with quadricovalent boron, was relatively

Table II. Stability of Compounds in the Vapor Phase

Fluorine Compd.[a]	Decompn. Temp., ° C.	Identification Products	Method
Hexafluorobenzene	>650	. . .	. . .
Perfluorocyclobutane-perfluoroisobutylene	670	Increase in perfluoroisobutylene	Gas chromatography
Tetrakis(perfluoromethyl)pyrazine	~650	C_2F_6(HCF_3 and SiF_4)	Infrared
Perfluorocyclohexane	620–650	Unsaturated fluorinated compound, possibly C_6F_{10}	Infrared
Cyanuric fluoride	530	Possibly CNF monomer	Infrared
2,4,6-Tris(perfluoromethyl)-*s*-triazine	480	CF_3CN	Infrared
Benzotrifluoride	430	HCF_3	Infrared
Perfluorodiethylcyclohexane	430	. . .	. . .
Nonfluorine Compd.[b]			
Quinoline	650	2,2′-Biquinoline	Ultraviolet
		Pyridine	Ultraviolet and gas chromatography
2,2′-Bipyridine	620–650	H_2, trace CH_4	Gas chromatography
Pyridine	620–650	. . .	. . .
Imidazole	620–650	. . .	. . .
Pyrimidine	620–650	H_2	Gas chromatography
Naphthalene	620–650	2,2′-Binaphthalene	Ultraviolet
Benzene	600	Biphenyl	Isolated
Thiophene	590–620	. . .	. . .
2-Phenylimidazole[c]	600	H_2	Gas chromatography
Benzonitrile	570–600	HCN	Infrared
		H_2	Gas chromatography
		2,4′-Bibenzonitrile	Isolated
Toluene	565–590	H_2 and CH_4	Gas chromatography
Benzothiazole	550–565	H_2	Gas chromatography
		H_2S	Lead acetate test
		2,2′-Bibenzothiazole	Isolated
Thiazole	540	H_2	Gas chromatography
		H_2S	Lead acetate test
Biphenyl	510–540	*p*-Terphenyl	Ultraviolet
Benzimidazole	400–430	. . .	. . .
1,2,4-Triazole	Under 430	NH_3, HCN	Infrared
		H_2	Gas chromatography
Indazole	Under 480	. . .	. . .

[a] All tests in Monel tube. [b] Vycor tube. [c] From 1-phenylimidazole by thermal rearrangement at 510–540° C. during test.

unstable. Products of decomposition at 360° and 510° C. have been analyzed by Florin and others (*8*). Loss of hydrogen occurred at the lower temperature and ring destruction only at the higher temperature.

Phosphorus Compounds. The data for five relatively stable phosphorus compounds are given in Table I. The order of stability was found as follows: triphenylphosphine oxide > triphenylphosphine (*4*) > tri-2-pyridylphosphine sulfide. As noted by Blake (*1*), triphenylphosphine oxide is probably more stable than the phosphine because the unshared electron pair is moved away from the phenyl rings where it weakens the C_{phenyl}—P bond. Sulfur also would contribute to stability in this way. The effect of the unshared electron pair of nitrogen in tri-2-pyridylphosphine sulfide apparently weakens the C—P bond and counteracts the effect of the sulfur.

Hexaphenylphosphorazole was less stable than hexaphenylborazole. A cyclic tetramer, diphenylphosphinic nitride tetramer, where phosphorus is in the quinquevalent state, was more stable than hexaphenylphosphorazole where phosphorus is in the trivalent state, probably because of the additional resonance stabilization in the tetramer.

Fluorinated Compounds. For greatest stability a perfluorinated compound is necessary. Perfluorinated aromatics are among the most stable organic compounds known. Perfluorination of an aliphatic skeleton increases stability appreciably. The stability of perfluorocyclobutane, which isomerized to perfluoroisobutylene (*2*) at elevated temperatures without decomposing or polymerizing, is exceptional. Perfluorocyclohexane also was very stable. Compounds with only isolated fluorines are not stabilized, and may decompose at lower temperatures than the basic structure because of the ease of loss of HF. The data given in Table II were obtained by vapor phase decomposition.

PRODUCTS OF DECOMPOSITION

Products of decomposition can be very complex. Madison and Roberts (*11*) found 21 products from the higher boiling condensation products of diphenylmethane where less than 5% of the sample was converted. Therefore, no attempt was made here to make a complete analysis of decomposition products. Those readily identified, usually from comparisons of infrared or ultraviolet spectra or by gas chromatography, are noted. Many products were identified from the ultraviolet spectra by a cancellation technique in which the sample was compared to a blank of undecomposed sample of appropriate concentration to cancel its spectrum and thus make the spectrum of the products more prominent.

The products identified were useful as indications of the paths of decomposition. Several thermal rearrangements occurred. Products identified and method of identification are listed in Tables II and III.

VAPOR PRESSURE DATA

The microisoteniscope is an ideal instrument for the determination of vapor pressures of a wide variety of liquid or solid compounds. It is especially valuable for use on research materials, since only about 300 mg. of sample is needed for a complete vapor pressure curve. The constants for the vapor pressure equation:

$$\log p_{\text{mm}} = b - \frac{a}{T(^\circ\text{ K.})}$$

for all the compounds measured in this instrument are recorded in Table IV.

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Table III. Products Formed in Condensed Phase Decomposition

Compd.	Decompn. Temp., ° C.	Identification	
		Products	Method
Naphthalene	570	2,2′-Binaphthalene	Ultraviolet
Biphenyl	543	*p*-Triphenyl	Ultraviolet
2-Phenylnaphthalene	507	2,2′-Binaphthalene	Ultraviolet
1,1′-Binaphthalene	452	Terrylene and perylene	Ultraviolet and visible
p-Quaterphenyl	482–504	1,1′,4′,1″,3″-Quaterphenyl[a]	Ultraviolet
2,2′-Bipyridine	482	Pyridine	Ultraviolet
Diphenyldiphenoxysilane	470–490	Diphenyl ether	Ultraviolet
Tetraphenylsilane	482	Biphenyl	Ultraviolet
Phenyl silicate	468	Phenol	Ultraviolet
2,2′-Bithiophene	474	Thiophene	Ultraviolet
Tri-2-pyridylamine	452	2,2′-Dipyridylamine	Ultraviolet and infrared
Ferrocene	454	Diferrocenyl	Isolated[b]
Phenazine	452–465	Aniline	Ultraviolet, infrared, and furfuraldehyde test
Diphenylmethane	454	Fluorene	Ultraviolet
1,10-Phenanthroline	432	Possibly 2 Alkyl-3-vinylpyridine	Ultraviolet, infrared, and bromine test
2-Phenoxypyridine	457	*N*-Phenyl-2-pyridone[a,c]	Isolated
Diphenylacetylene	421	Possibly 1,1,2,4-tetraphenylbut-1-ene-3-yne[a]	Isolated
		Methane	Infrared

[a] A rearrangement product. [b] Elemental analysis calculated for $C_{20}H_{18}Fe_2$: C, 64.9; H, 4.9. Found: C, 64.7; H, 5.0. Infrared had adsorptions characteristic of monosubstituted ferrocenes. Compound was recently reported (*10*). [c] Rearrangement at red heat reported (*14*).

Table IV. Vapor Pressure Data

Comp.	Constants *a*	Constants *b*	° C., Vapor Pressure, 1 Atm.[a]
1,3,5-Triphenylbenzene, above 390° C.	4048	8.376	464
Hexaphenylbenzene, above m.p.	4444	8.444	525
Hexaphenylbenzene, solid	8550	14.056	...
Tri-*o*-phenylene, above 370° C.	3527	7.7725	448
Coronene, liquid	5362	9.193	576
Coronene, solid	5764	9.761	...
1,5,9-Tripyridinobenzene, above 375	3521	7.8662	433
1,2,6-Tripyridinobenzene, above 375	3400	7.687	434
Triphenyl-*s*-triazine, liquid	4650	9.164	467
Hexaphenylmelamine, liquid	6860	11.19	554
Cyanuric tricyanide, liquid	4040	10.80	237
Hexaphenylphosphazole	4000	8.44	447
Hexaphenylborazole, liquid	4990	9.280	511
Hexaphenylborazole, solid	6450	11.410	...
2,2′-Biquinoline	3720	8.00	453
Diphenylcarbodiimide	3425	8.59	326

[a] Calculated from the vapor pressure–temperature equation assuming no decomposition.

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Stability of Acetylene

Energy for Ignition of Liquid Acetylene by Sparks between Submerged Electrodes

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THE SENSITIVITY of liquid acetylene to various types of ignition stimuli has received considerable attention (*4,7*). One of the more reproducible tests for obtaining sensitivity data on liquid and solids is the standard card gap test (*1, 3*), in which varying numbers of cards are placed between an initiator explosive and the sample under consideration. Complications arise when the liquid has a vapor pressure greater than 1 atm., as is the case with liquid acetylene. During the work described, the ignition stimulus was provided by a spark passed between electrodes submerged in the liquid. Energy was conveniently imparted to the liquid sample, which was re-used when no explosion resulted. The energy is given by $\frac{1}{2} CV^2$, where C is the capacitance of the capacitor storing the electrical energy and V is the voltage to which it is charged before being discharged across the spark gap. By starting at low energies and proceeding to higher ones, it was possible to determine a threshold below which no ignition occurred and above which ignition normally occurred. When no ignition resulted from the passage of a spark through the liquid, the spark was easily visible through an optical system.

The object of this work was to study the ignition energy of liquid acetylene as a function of electrode gap, electrode voltage, temperature, pressure, and diluents. Agitation was found to affect the sensitivity and was also investigated.

From spark ignition studies on gaseous explosives, it has been found that in general the minimum energy required for ignition varies with electrode distance (for pointed electrodes), as shown in Figure 1 (*8*). Below a certain distance, known as the quenching distance, d, the ignition energy increases sharply. For a relatively large range at increasing spark gaps, the energy remains constant at a low value, H. This minimum in the curve is called the "minimum ignition energy." Photographs (*8*) have shown that the spark energy is imparted to the gas at a point roughly halfway between the electrodes. For very large electrode gaps, the energy is apparently distributed over a longer path and the ignition energy again rises.

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