

Table IV. Vapor Pressure Data

Comp.	Constants		° C., Vapor Pressure, 1 Atm. ^a
	a	b	
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- <i>o</i> -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- <i>s</i> -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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Because of the rapidity and small volume of the spark discharge, it is assumed to be a thermal source.

To visualize in a simple manner what happens when spark ignition occurs (9), consider an adiabatic combustion wave traveling down a tube. The enthalpies in front of and behind the combustion front are the same, but the front itself contains a certain excess enthalpy, h , which is necessary to support the combustion. In the case of spark ignition, a combustion wave radiates spherically from the point at which the spark occurs, the area of this front increasing rapidly. As the flame front expands from r to $r + dr$, the wave-front area increases by a factor of $2 dr/r$. Since excess enthalpy is required to propagate the flame front and also to expand the area, the ignition source will have to supplement the energy liberated in the wave or the flame will die out. The increment of excess enthalpy per unit area is approximated by

$$dh = h \times \frac{2 dr}{r}$$

so that

$$\frac{dh}{dr} = \frac{2h}{r}$$

This will have a large value near the origin and vanish for large radii. This means that the ignition source must supply enough energy for the flame front to propagate to a certain diameter, d , beyond which the front becomes self-sustaining. In the case of a liquid explosive, this self-sustaining combustion wave can then rapidly accelerate and turn into a detonation wave. This view-point explains why closely spaced electrodes increase the ignition energy. They project into the sphere of diameter d , and remove heat that is being used by the rapidly expanding combustion wave.

In experiments with liquid acetylene, the general features described above for gaseous explosives are also observed with this liquid explosive. However, the voltages necessary to pass a spark between electrodes immersed in an insulating liquid are higher than those for gases and the energies involved are greater.

EXPERIMENTAL

The acetylene was from a WK cylinder containing acetylene dissolved in acetone. To store it before use and

to remove traces of water and acetone, the acetylene was first transferred from the cylinder to a vessel filled with activated silica gel. Mass spectrometer analysis of the gas desorbed from this vessel showed the following impurities: methane 1.2%, nitrogen 0.6%, argon 0.01%, oxygen 0.10%, and diacetylene 0.02%. Since most of these impurities are more volatile than liquid acetylene, a small amount of liquid acetylene was evaporated and discarded before each experiment was started. The vapor pressure of the resulting liquid agreed with literature values.

Figure 2 is a photograph of a typical vessel in which spark ignition of liquid acetylene was carried out. Expendable glass vessels of 2.5-ml. volume were used as a matter of convenience; they were connected to other parts of the system by a glass-metal seal. These were constructed from heavy-walled borosilicate glass tubing and were capable of withstanding pressure of 400 p.s.i.g. The electrodes were $\frac{1}{16}$ -inch tungsten rods with pointed ends. For a typical run, 1.5 ml. of liquid was added to the vessel by cooling it and condensing the gas under pressure. Considering the volume of liquid acetylene employed, the explosions were severe. Precautions were taken to prevent trichloroethylene from the bath from being scattered over a 20-foot wall surrounding the apparatus.

Figure 3 is a diagram of the cooling bath and associated equipment. The space between the insulating outer jacket and the trichloroethylene cooling bath was filled with dry ice to provide approximately constant cooling. By regulating the current through the heater, the temperature of the bath could be held constant for short periods at any temperature between 0° and -78° C. Magnetic stirring was employed. A 6-volt light bulb in the bath provided illumination, and the vessel was observed through a periscope. The current was conducted to the electrodes by insulated No. 14 solid copper wire.

Figure 4 is a diagram of the electrical apparatus used to generate the sparks. After the capacitor was charged to a certain voltage, V , the remote switch controlling the two relays was thrown. This opened switches S_2 and S_4 , and closed switch S_3 a fraction of a second later. The high potential at the grid of the low resistance 5C22 hydrogen thyratron placed it in the conducting state and grounded the high voltage side of the capacitor, C . This caused the pulse of current to flow through the primary of the 1 to 3 step-up pulse transformer and resulted in

Figure 2. Sample vessel

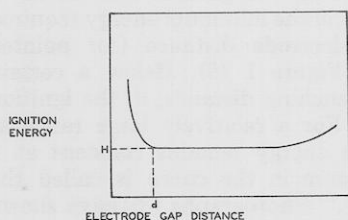


Figure 1. Variation of minimum ignition energy with electrode gap distance

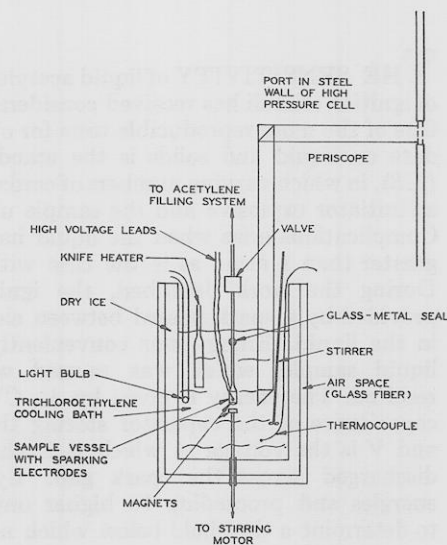
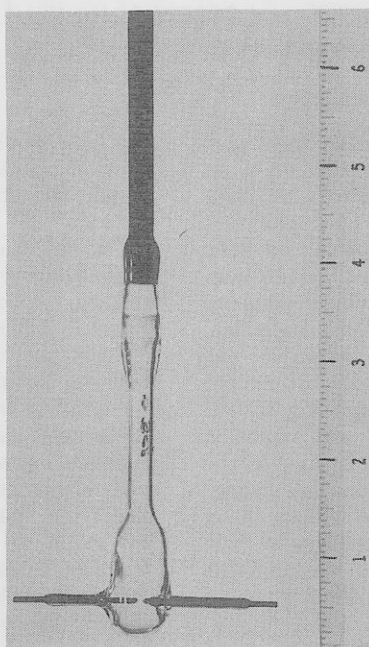


Figure 3. Cooling bath and associated equipment

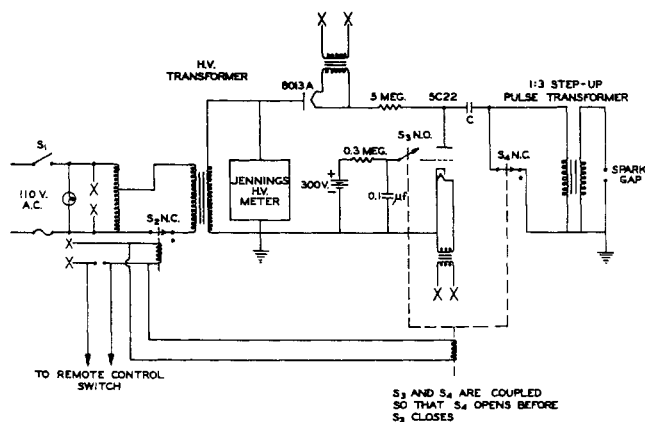


Figure 4. Electrical apparatus

the energy being dissipated in the spark gap. Because of the pulse transformer, the energies employed were probably less by a constant factor than those indicated by the values of C and V . With this system sparks could be passed between the electrodes at voltages greater than those necessary for the breakdown of the insulating liquid.

The procedure employed during a single determination was to increase the voltage gradually and close the switch discharging the capacitor at 1000-volt intervals. Voltages at which a spark jumped the gap and the explosion occurred were recorded. The passage of a spark when no explosion resulted was easily visible through the periscope. A large energy range could be covered by changing capacitors.

RESULTS AND DISCUSSION

Variation of Ignition Energy with Electrode Gap. In initial experiments the variation of the spark ignition energy with temperature was measured. Because of the spark energies available, -30°C . was a convenient temperature for experiments with liquid acetylene. Table I illustrates the variation of the ignition energy with electrode gap.

The data indicate that variation of ignition energy with electrode gap is much the same for liquid acetylene as for gases. The ignition energies are relatively high for large and small spark gaps, but they were low for an intermediate range of gaps. It appears from the data that the quenching distance is about 0.05 to 0.08 cm., and that the minimum ignition energy is near 0.7 joule. Electrode gaps of approximately 0.08 cm. were used in other experiments at -30°C .

As was expected, the quenching distance increased with decreasing temperature. No ignition occurred at -40°C . with a gap of 0.058 cm. at 5.3 joules, whereas 4.2 joules was sufficient with a gap of 0.102 cm.

Variation of Minimum Ignition Energy with Electrode Voltage. The expression for the spark energy is $\frac{1}{2} CV^2$, where C is the capacitance of the capacitor storing the electrical energy and V is the minimum voltage at which ignition takes

Table I. Variation of Ignition Energy with Electrode Gap at -30°C .

Electrode Gap, Cm.	Min. Ignition Energy, J.
0.025	> 5.3
0.036	> 0.85
0.058	0.61
0.076	0.69 ^a
0.084	0.066
0.086	1.0
0.229	1.8

^a Average of 5 determinations. Results range from 0.50 to 0.85.

place. If the spark behaves as a thermal ignition source, one would expect that the minimum ignition energy would be independent of C and V . To determine whether or not this was true, the capacitance values were varied so that ignition occurred in various voltages.

The experiments were conducted with the electrodes immersed in liquid acetylene at -30°C . and with gaps of about 0.08 cm. (Table II).

Although the first result was higher than any of those observed using the 0.01- μf . capacitor, there did not seem to be any general trend as the voltage was increased from 27 to 47 kv. In the last case, the maximum voltage available was not enough to reach the minimum ignition energy. It was concluded that, for the purpose of this work, ignition energy could be regarded as independent of V .

Variation of Minimum Ignition Energy with Temperature. The data in Table III illustrate the rapid change of the minimum ignition energy with temperature.

Above -27°C . the energies were too low for measurement with the available apparatus; below -50°C . they increased rapidly to greater than 11 joules at -78°C . Hence, one of the best means of desensitizing a liquid-acetylene system would be to keep the liquid cold.

Carbon Formed by Sparks in Liquid Acetylene. When a spark was passed through liquid acetylene, a small amount of carbon appeared even when no explosion resulted. Apparently, some of the acetylene had decomposed, but the decomposition did not proceed far enough to become self-sustaining. To determine the quantity of carbon formed, 25 sparks of 11-joules energy each were passed through liquid acetylene at -78°C . and the residual carbon was collected and weighed. The pertinent data follow:

Total weight of carbon formed, mg.	0.7
Weight of carbon per spark, mg.	0.03
Diameter of sphere of liquid C_2H_2 containing this weight of carbon, cm.	0.05

If one assumes that a spherical combustion has taken place and that all of the acetylene in the sphere was converted to carbon and hydrogen, the diameter of the sphere through which the reaction passed was about 0.05 cm. Even allowing for some inefficiency in the electrical circuit, this is a small amount of decomposition for such a high energy input. Part of the spark energy, as well as the heat of reaction of the decomposed acetylene, must have been removed by conduction through the acetylene.

Comparison of Ignition Energies for Liquid and Vapor. During these experiments it was determined that the minimum ignition energy for the vapor in equilibrium with liquid acetylene at -30°C . was less than 0.10 joule, as opposed to 0.68 joule for the direct ignition of the liquid. Under the proper conditions, the vapor phase decomposition propagated into the liquid. It is probable that an explosion of the liquid at -30°C . results from ignition of the vapor and propagation into the liquid rather than from direct ignition of the liquid.

The ignition of most liquid explosives is generally assumed (2) to occur by way of adiabatic compression of small bubbles, or by some similar mechanism (6). This leads to high temperatures, either igniting the liquid directly or igniting the vapor with a resultant propagation into the liquid. Spark ignition is very similar to ignition by the adiabatic compression of bubbles, since in each case the explosion propagates from a small hot spot.

Effect of Pressure and Agitation on Minimum Ignition Energy of Liquid Acetylene. The application of pressure by means of an inert gas increased the ignition energy of the liquid. Stirring the liquid increased its sensitivity and decreased the minimum ignition energy. Data illustrating both of these effects are given in Table IV.

Table II. Variation of Minimum Energy with Electrode Voltage at -30°C .

$C, \mu\text{f.}$	Voltage ^a Explosion, Kv.	Min. Ignition Energy, J.
0.025	27	1.0
0.01	33	0.68 ^b
0.008	41	0.74
0.005	No explosion at 47	> 0.60

^a Voltage at secondary of 1 to 3 step-up transformer.

^b Average of 7 tests. Results range from 0.50 to 0.87.

Table III. Variation of Minimum Ignition Energy with Temperature

Temp., $^{\circ}\text{C}$.	Vapor Pressure of Acetylene, P.S.I.A.	Min. Ignition Energy, J.
-27	179	0.13
-30	160	0.68 (av. of 7 tests)
-35	135	0.98
-40	113	Between 0.98 and 4.1
-50	78	1.5
-78	21	> than 11

Table IV. Effect of Pressure and Agitation on Minimum Ignition Energy of Liquid Acetylene at -30°C .

Pressurizing Gas	Vapor Pressure = 160 p.s.i.a.		Min. Ignition Energy, J.
	Total Pressure, P.S.I.A.	Agitation	
None	160	No	0.68 ^a
None	160	Yes	0.39
Argon	215	No	1.5
Nitrogen	215	Yes	1.1
Carbon monoxide	415	Yes	5.6
Helium	415	No	11.0
Helium	415	Yes	0.13

^a Average of 7 tests. Results range from 0.50 to 0.85 joule.

There is a slight increase in the ignition energy with a relatively small additional argon pressure. There was a notable increase in the ignition energy in the case where 225 p.s.i. of helium pressure was applied in excess of the 160-p.s.i.a. vapor pressure of the liquid acetylene. In this latter case, the decrease in the ignition energy on stirring was most noticeable. This same effect was also observed for the liquid acetylene under its own vapor pressure. Ignition energies for the stirred samples under nitrogen and carbon monoxide were greater than those for the unstirred acetylene alone. The difference in behavior may be due to the differences in solubility of the pressurizing gases in liquid acetylene.

The sensitization resulting from stirring is probably related to bubble formation, mentioned above. Any liquid would be expected to contain a large number of microscopic bubbles (5). Experimental conditions may affect the number and size of the bubbles in liquid acetylene and either increase or decrease the explosive sensitivity. Stirring may create more bubbles or it may circulate dust particles so that they serve as nuclei for bubble formation when a spark is passed between the electrodes. Gas in the bubble may be ignited by the spark and the explosion then propagated into the liquid. Increasing the pressure may decrease the number of bubbles or make them small enough so that they are less likely to play a role in the ignition.

Effect of Diluents. By adding diluents to the liquid, it was considered possible to determine whether an explosion was initiated in the liquid or in the vapor that was formed momentarily when a spark was passed through the liquid. If the decomposition started in the vapor phase, a diluent with a low vapor pressure should show a relatively small effect, whereas one with a volatility similar to that of

acetylene should have a larger effect. Table V shows the results when the liquid was diluted with acetone, carbon dioxide, and ethylene. In each case the sample was stirred during the experiment.

Acetone, with its low vapor pressure, did not produce the same marked increase in the ignition energy as was observed for the carbon dioxide and ethylene. Each of these has a vapor pressure of the same order of magnitude as that of acetylene at -30°C ., 160 p.s.i.a. Ignition of the liquid apparently is associated in the same manner with an initial decomposition in the vapor phase, since the two diluents with appreciable vapor pressures provided as much greater increase in the ignition energy than acetone. These results are consistent, therefore, with those concerning the effect of agitation and pressure.

Table V. Effect of Diluents (Plus Agitation) on Ignition Energy of Liquid Acetylene at -30°C .

Diluent	Vapor Pressure at -30°C ., P.S.I.A.	Weight % in Solution	Min. Ignition Energy, J.
Acetone	0.2	20	0.4
Acetone	0.2	35	4.2
Carbon dioxide	207.0	25	> 11
Ethylene	270.0	20	> 11

CONCLUSIONS

The spark-ignition energy of liquid acetylene at -30°C . varies in a manner similar to that commonly observed for explosive gas mixtures. The minimum ignition energy and quenching distance increase with decreasing temperature.

The minimum ignition energy for the vapor is lower than that for the liquid at -30°C ., indicating that decomposition starts in vapor "bubbles" and propagates into the liquid. This is substantiated by the fact that a diluent with a high vapor pressure increases the ignition energy to a greater degree than one with a low vapor pressure.

Agitation of liquid acetylene results in a lower ignition energy, whereas excess pressure applied by means of an inert gas increases the ignition energy. Both effects can be explained on the basis of an initial reaction in vapor bubbles.

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