CONCLUSIONS

Seventeen cyclic sulfides were identified in a 111° to 150° C. fraction of Wasson, Tex., crude oil. This brings to 21 the total number of this class of sulfur compounds found in Wasson crude oil by the research staff of the Bureau of Mines-API Research Project 48.

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LITERATURE CITED

(1) Ball, J.S., Rall, H.T., *Proc. Am. Petrol. Inst. Sect. III* **42**, 128–45 (1962).
(2) Birch, S.F., *J. Inst. of Petrol.* **39**, 185–205 (1953).
(3) Coleman, H.J., Thompson, C.J., Hopkins, R.L., Rall, H.T., J. CHEM. ENG. DATA **10**, 80–4 (1965).
(4) Cox, E.R., *Ind. Eng. Chem.* **15**, 592–3 (1923).
(5) Donnell, C.K., Kennedy, R.M., *Proc. Am. Petrol. Inst. Sect. III* **26**, 23–31 (1946).
(6) Mabery, C.F., Quayle, W.O., *J. Soc. Chem. Ind.* **19**, 505–6 (1900); *Am. Chem. J.* **35**, 404–32 (1906).
(7) Polly, O.L., Byrns, A.C., Bradley, W.E., *Ind. Eng. Chem.* **34**, 755–8 (1942).
(8) Thierry, E.H., *J. Chem. Soc.* **1925**, pp. 2756–9.
(9) Thompson, C.J., Coleman, H.J., Hopkins, R.L., Rall, H.T., J. CHEM. ENG. DATA **9**, 473–9 (1964).
(10) Thompson, C.J., Coleman, H.J., Ward, C.C., Rall, H.T., *Anal. Chem.* **32**, 424–34 (1960).

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Hot Surface Ignition Temperatures of Hydrocarbon Fuel Vapor-Air Mixtures

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Autoignition temperatures (AIT's) and "wire" ignition temperatures of various hydrocarbon combustibles were determined as a function of heat source dimensions using stagnant or near-stagnant combustible vapor-air mixtures. The combustibles included *n*-hexane, *n*-octane, *n*-decane, JP-6 jet fuel, and an adipate ester aircraft engine oil (MIL-L-7808). Generally, the ignition temperatures obtained with heated Pyrex vessels and Nichrome wires or rods and tubes varied little with fuel-air ratio except at low ratios where they tended to increase. Consistent with thermal ignition theory, the ignition temperatures increased with decreasing heat source dimensions, but they correlated over a greater range of source dimensions when the surface area of the heat source rather than the radius was used. The best correlation was obtained with high AIT combustibles.

MINIMUM ignition temperatures of combustible mixtures are often determined for safety purposes under heating conditions where the energy source for ignition is a heated surface. In this connection, minimum autoignition temperatures (AIT's) are particularly useful and have been determined for many combustible materials (*1, 6, 17*). They are ordinarily determined under quiescent conditions in heated vessels sufficiently large to minimize wall quenching; under such conditions, the fuel contact times or ignition delays tend to be maximum, and the rate of heat input is not important. However, AIT values increase as the size of the vessel and the fuel contact time are decreased (*11, 14*). With a sufficiently small heat source, such as a fine heated wire, the heat input rate becomes an important factor. Generally, the ignition temperatures of combustible mixtures determined with heated wires or rods also increase with decreasing contact times and heat source dimensions (*5, 9, 10*). Surprisingly, little quantitative information is available for most combustibles on the correlation of these "hot surface" ignition temperatures over a wide range of heat source dimensions. The works of Silver (*16*) and Paterson (*12*) are noteworthy in this respect, but the relationships they obtained were primarily applicable to small platinum and quartz spheres.

The present work was initiated to define the hot surface ignition temperatures of various hydrocarbon fuel vapor-air mixtures and to obtain relationships which may be used to predict the ignition of the combustible mixtures when in contact with heated surfaces of various dimensions. The heat sources consisted of heated cylindrical and spherical Pyrex (No. 7740) vessels and Nichrome wires and rods or tubes. Since minimum ignition temperatures were of primary interest, stagnant and near stagnant flow conditions were employed. According to thermal ignition theory (*4, 15*), the temperature at which ignition occurs should vary inversely as a logarithmic function of the heat source size. Thus, autoignition and wire ignition temperatures, such as those determined here, should agree when the heat sources are of equivalent size; admittedly, the mode of heat transfer and the reaction kinetics can be limiting factors. In the present work, the ignition temperatures appeared to correlate over a greater range of heat source dimensions when the surface area of the heat source rather than the radius was used. The combustibles included *n*-hexane, *n*-octane, *n*-decane, a hydrocarbon jet fuel (JP-6), and an adipate ester aircraft engine oil (MIL-L-7808).

EXPERIMENTAL APPARATUS AND PROCEDURES

Autoignition temperatures of the combustibles of interest were determined in quiescent air using a modified ASTM ignition temperature apparatus (*17*). For these determinations, the apparatus was fitted with cylindrical Pyrex vessels 15 cm. long and between 0.4 and 1.75 cm. radius (7.5 to 135 cc. in volume); spherical vessels between 1.0 and 3.7 cm. radius (5 to 213 cc. in volume) were also used. The determinations were made under constant pressure conditions although the reaction vessels were covered with a watch glass after adding the combustible. The vessel temperature, the fuel residence time, and the volume of liquid fuel injected into the vessel were varied to obtain the minimum temperatures for ignition. Since the lowest and most reproducible AIT values are ordinarily obtained by conditioning the vessel surface with an ignition, this practice was employed in these determinations. In all cases, ignition was evidenced by flame visible to the naked eye. Generally, the ignitions were the hot flame type although a few were borderline and possibly the cool flame type. The AIT values were repeatable within ±2½° at low temperatures (about 250° C.) and ±10° at high temperatures (about 550° C.).

Wire Ignition Temperature Experiments. Wire ignition temperatures of the combustibles were determined under flow conditions in the apparatus shown in Figure 1 using electrically heated Nichrome wires of 0.02 to 0.13 cm. radius; Nichrome rods and Inconel tubes of 0.25 to 1.27 cm. radius were used to obtain data at larger radii. The apparatus was equipped with liquid fuel- and air-feed assemblies capable of providing premixed fuel vapor-air mixtures at a uniform rate to a heated reaction chamber—a Pyrex tube 5 cm. I.D. and 20 cm. long mounted in a small oven. Two side arms at the middle of the reaction chamber are fitted with brass adapters for use in mounting the wires (or rods and tubes) normal to the direction of flow. A 5-cm. length of wire is heated electrically between the adapters.

To conduct an experiment, the wire is first heated to a predetermined surface temperature which is measured with an optical pyrometer. The fuel vapor-air mixture is then passed over the heated wire at a designated flow rate and, depending on whether or not ignition occurs, the wire temperature is decreased or increased in succeeding trials until the lowest temperature for ignition is found. Minimum ignition temperatures were generally repeatable to within ±10°. Here, the wires were also conditioned with an ignition and were replaced when changing fuels and when the data appeared anomalous. In each case, ignition was evidenced by the appearance of flame and by a sudden rise of the gas mixture temperature; little preignition reaction was observed until a sudden temperature rise, which was always accompanied by visible flame. Gas mixture temperatures were measured with two Chromel-Alumel thermocouples (28-gage) located 2.5 cm. above and below the heated wire and were recorded continuously on a galvanometer oscillograph during each run.

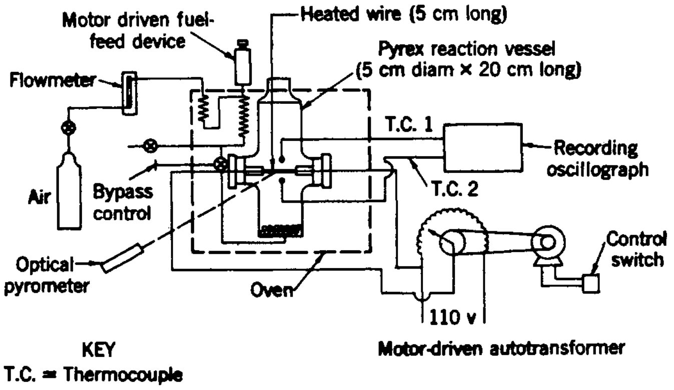

Figure 1. Wire ignition temperature apparatus

In the experiments with Inconel tubes, small cylindrical heaters were inserted into each tube to heat it to the desired temperature; about 3 cm. of the 5-cm. heated section was usually at near uniform temperature. Each of the tubes was also equipped with a thermocouple to measure surface temperatures below the operating range of the optical pyrometer (600° to 2900° C.). These thermocouples were spot-welded on the surface at the midpoint of each tube. According to calibration data obtained above 600° C., temperatures measured with the thermocouples were usually 10° to 15° lower than those measured with the pyrometer.

Most of the experiments were conducted at a mixture flow rate of 290 cc. per minute (NTP conditions of 15° C. and 1 atm.). The initial mixture temperature was 150° C. (maintained by the oven) in the runs with the fuels and 260° C. in those with the MIL-L-7808 engine oil; corresponding mixture velocities at these temperatures were 0.35 and 0.45 cm. per second, respectively. A higher mixture temperature was used for the engine oil than for the fuels because of the former's higher boiling constituents, primarily adipate diesters, which vaporized at temperatures between 250° and 420° C. The viscosity of this oil was 12.1 cs. at 38° C., and its flash point was 225° C. The JP-6 jet fuel contained about 85% saturated hydrocarbons and 14% aromatic hydrocarbons; hydrocarbons with 9 carbon atoms predominated. Viscosity of this fuel was 1.17 cs. at 38° C.; its flash point was approximately 36° C. All of the neat hydrocarbon fuels were at least 99% pure.

RESULTS AND DISCUSSION

Autoignition Temperatures of Quiescent Mixtures. The minimum autoignition temperatures found for the hydrocarbon fuels and engine oil in the cylindrical and spherical Pyrex vessels are given in Table I. Also included for comparison are corresponding AIT's found using a 200-cc. Pyrex Erlenmeyer, the vessel recommended for conducting such determinations by the modified ASTM method (*17*). The apparent fuel-air weight ratio required to obtain most of these ignition temperatures was 0.35 ±0.1; this ratio is much greater than the stoichiometric value (<0.07 required for complete combustion of the neat fuels. Uniform mixtures of these combustibles in air normally would not be expected to propagate flame at such high fuel-air ratios except as cool flames. As reported in similar AIT determinations (*13*), the effect of fuel-air ratio on AIT was most pronounced at low ratios and decreased with increasing temperature. At the same time, ignition of the combustible vapor-air mixtures was increasingly more difficult to achieve with a decrease in heat source dimensions.

To illustrate the effect of vessel dimensions, the ignition temperatures found in the cylindrical and Erlenmeyer vessels (7.5 to 200 cc. in volume) are plotted in Figure 2*A* *vs.* the surface area to volume ratio (S/V) of the vessel employed. Since vessel length was constant (15 cm.) excluding the Erlenmeyer, this figure essentially shows the effect of vessel radius (r) on ignition temperature. The AIT's, particularly for the neat hydrocarbon fuels and JP-6 fuel, increased sharply when the S/V ratio was in excess of about 2.0 cm.$^{-1}$; this ratio corresponds to a vessel volume of 60 cc. and a radius of 1.13 cm. Below this critical S/V ratio, the effect of vessel dimensions was slight. Such results are expected since surface effects and heat losses to the vessel walls should be most critical for ignition in the smallest size vessels.

The AIT values obtained with the *n*-hexane, *n*-octane, and *n*-decane fuels increased consistently with decreasing molecular weight. In addition, the variation with vessel

Table I. Minimum Autoignition Temperatures of the Hydrocarbon Fuels and an Engine Oil in Cylindrical and Spherical Pyrex Vessels with Quiescent Air at Atmospheric Pressure

(Ignition criterion-appearance of flame)

Vessel Volume, Cc.	Vessel Radius, Cm.	S/V^a, Cm.$^{-1}$	S, Cm.^{2}	Autoignition Temperature, ° C. *n*-Hexane	*n*-Octane	*n*-Decane	JP-6	Engine oil MIL-L-7808
Cylindrical Pyrex vessels (15-cm. length)								
7.5	0.40	5.15	38.5	629	603	602	596	580
10	0.46	4.50	45.0	603	583	587	558	557
23	0.70	2.95	68.5	541	505	490	484	473
41	0.95	2.25	91.4	431	382	373	408	445
45	1.00	2.15	96.8	432	382	322	375	441
60	1.13	1.95	117	266	232	224	244	424
135	1.75	1.25	171	265	227	214	242	421
Pyrex Erlenmeyer (12.7-cm. length)								
200	(2.24)^b	(0.92)^b	184	234	220	208	232	404
Spherical Pyrex vessels								
5	1.06	2.85	14.1	599	551	537	539	549
10	1.33	2.25	22.5	509	469	427	429	471
15	1.53	1.95	29.4	491	445	409	403	433
33	1.98	1.50	49.9	337	279	255	273	415
50	2.28	1.30	65.8	299	261	242	259	415
104	2.92	1.03	107	253	231	217	253	403
213	3.72	0.80	172	239	226	215	243	401

[a] Surface area to volume ratio of vessel. [b] Equivalent values of a 200-cc. cylinder.

radius was similar to that observed for JP-6 but much greater than that for the aircraft engine oil. The AIT values for the engine oil in the large vessels (≧ 1.13 cm. radius) were higher than those for the fuels, whereas the opposite trend was found in vessels of less than 0.95 cm. radius—i.e., at temperatures above about 450° C. Apparently, the adipate esters, which largely make up this oil, break down to form more thermally unstable species with increasing temperature than do the hydrocarbon fuels. Thus, the order of thermal stability determined for combustibles from their autoignition behavior at low temperatures is not necessarily the same as that at high temperatures.

Minimum AIT's of each of the combustibles were generally lower in small spherical Pyrex vessels (< 60 cc.) than in cylindrical ones of comparable volumes because of the smaller S/V ratios of the spheres. However, the AIT's varied little with vessel shape for vessels greater than about 60 cc. in volume. Figure 2*B* shows a plot of the data obtained with spherical vessels of 5 to 213 cc. volume. The critical S/V ratio above which vessel size effects were pronounced was about 1.5 cm.$^{-1}$ as compared to 2.0 cm.$^{-1}$ in the case of the cylindrical vessels. With Erlenmeyer vessels, AIT's ordinarily tend to fall between those obtained with cylindrical and spherical vessels of similar volumes. Figure 3 shows such a comparison of AIT data for *n*-decane; here the values obtained with the Erlenmeyers are less than those found with the cylindrical vessels but nearly the same as those for the spheres. The data above show that vessels greater then 60 cc. in volume should be used in minimum AIT determinations at atmospheric pressure.

Wire Ignition Temperatures of Quiescent and Flowing Mixtures. The ignition temperature data obtained for the hydrocarbon fuels and engine oil with heated Nichrome wires and rods or tubes are summarized in Table II for the flow rate of 290 cc. per minute (NTP). The variation of wire ignition temperature with fuel-air weight ratio (0.05 to 0.5) and wire radius (0.02 to 0.13 cm.) was similar for each combustible; Figure 4 shows the trend observed with *n*-hexane vapor-air mixtures. Fuel-air ratio is of little influence here except at low ratio values where the ignition temperatures tend to increase appreciably. These data are similar in many respects to those found with the heated vessels. The ignition temperature values increase with a decrease in heat source

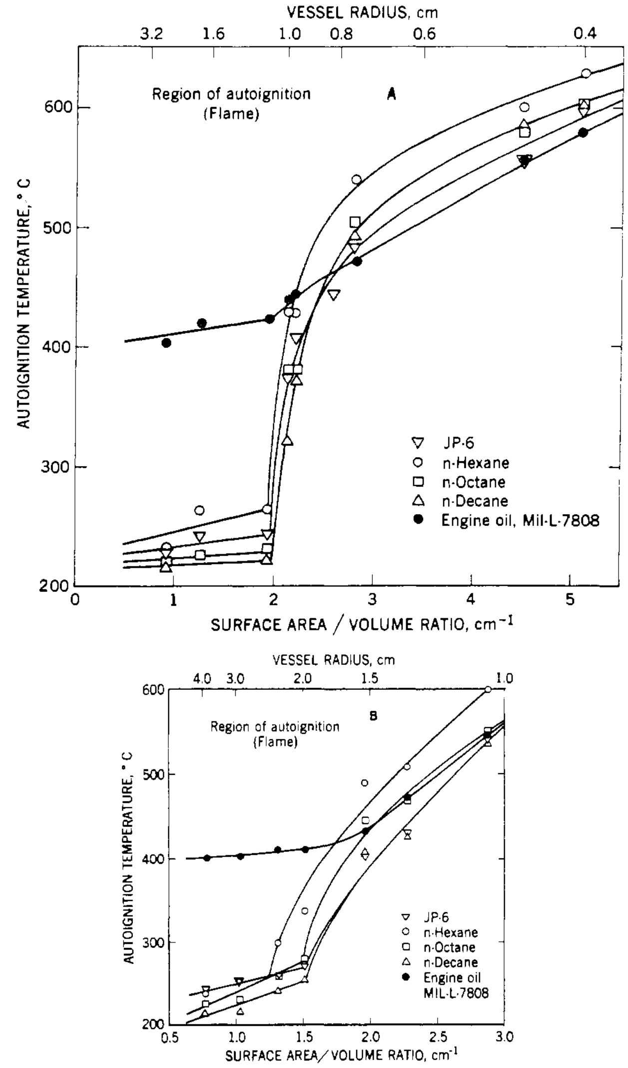

Figure 2. Effect of vessel surface area-to-volume ratio on minimum autoignition temperatures of hydrocarbon fuels and engine oil in quiescent air

A. Pyrex cylinders, 15-cms. long; B. spherical Pyrex vessels

Table II. Minimum Hot Surface Ignition Temperatures of the Hydrocarbon Fuels (150° C.) and an Engine Oil (260° C.) in Air at a Mixture Flow Rate of 290 Cc. per Minute (NTP)

(Ignition criterion, appearance of flame; Pyrex reaction vessel, 5 cm. I.D., 20 cm. long)

Radius of Heat Source, Cm.	Surface Area of Heat Source, Cm.^{2}	Ignition Temperature, ° C.				
		n-Hexane	*n*-Octane	*n*-Decane	JP-6	Engine oil MIL-L-7808
		Nichrome wires (5-cm. length)				
0.020	0.65	996	993	968	1026	843
0.041	1.30	938	909	889	966	702
0.063	2.05	866	816	782	899	691
0.102	3.30	853	780	760	831	627
0.129	4.15	833	782	735	838	631
		Nichrome rods and Inconel tubes (5-cm. length)				
0.25	8.3	760	738	721	780	645
0.64[a]	20.3	643	641	627	668	560
0.95[a]	30.4	571	538	560	585	546
1.27[a]	40.5	516	528	515	530	543

[a] Dimensions apply to outside surface of Inconel tubes over which combustible mixture was passed.

radius and molecular weight of the neat hydrocarbon fuels; also minimum values occurred at high fuel-air ratios (between 0.3 and 0.5). Furthermore, the values for the engine oil are lower than those for any of the four hydrocarbon fuels; this behavior is consistent with that observed in the AIT experiments with cylindrical vessels less than 0.95 cm. radius. However, the wire ignition temperatures for the JP-6 fuel are generally higher than those for *n*-hexane, whereas the opposite is the case in the autoignition experiments. No explanation for this trend is evident at this time. Also, the ignition temperatures found for the combustibles with large heating elements (0.6 to 1.3 cm. radius) are comparable with those obtained with small cylindrical heated vessels (0.4 to 0.7 cm. radius).

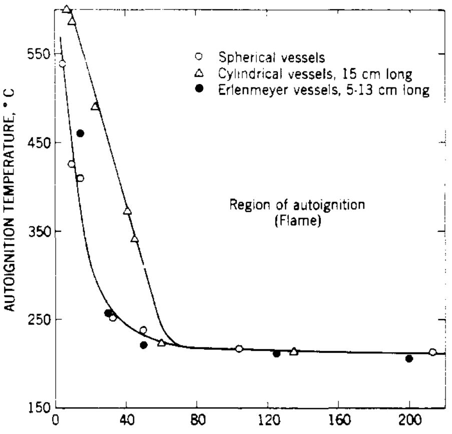

Figure 3. Comparison of minimum autoignition temperatures of *n*-decane in quiescent air for various size spherical, cylindrical, and Erlenmeyer Pyrex vessels

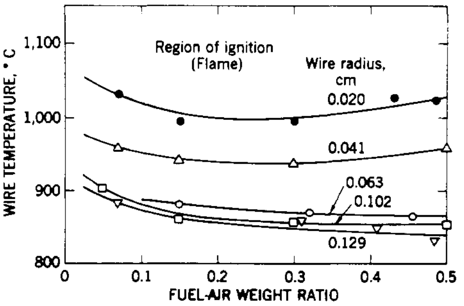

Figure 4. Wire ignition temperatures of *n*-hexane vapor-air mixtures at 150° C.

As in the AIT experiments, the minimum ignition temperatures were found when ignition delay times were maximum (≧ 10 seconds). The delay times and the gas mixture temperature rises at ignition generally increased with decreasing fuel-air ratio or as the stoichiometric ratio was approached. Temperature rises owing to preignition reaction were negligible or at least not detected by the thermocouples positioned 2.5 cm. above and below the wire. These temperature rises are more noticeable with branched chain and aromatic hydrocarbons than with straight chain hydrocarbons (*1*), such as hexane, octane, and decane fuels of this work.

Although wire ignition temperatures normally increase with the velocity of the combustible mixture, the velocity effect was not great for the range of velocities used in the present work. Figure 5 shows that the minimum ignition temperatures for the hydrocarbon fuels at the flow rate of 290 cc. per minute (0.35 cm. per second) are the same or slightly higher than those found under quiescent conditions with most of the heating elements used. In one

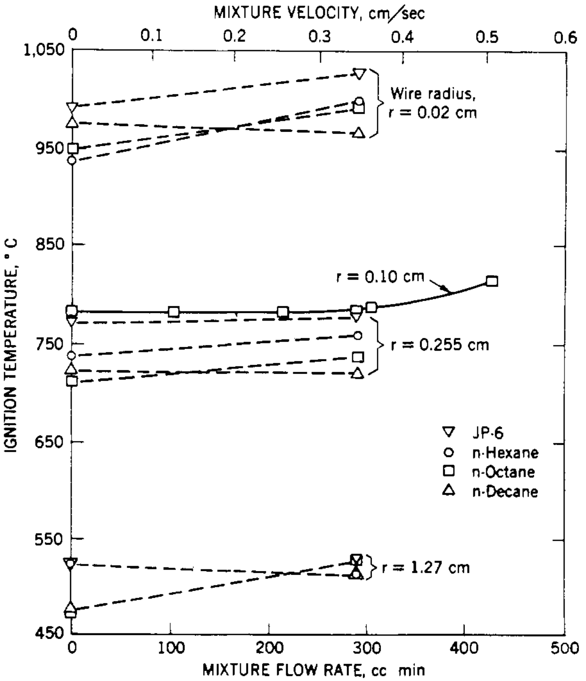

Figure 5. Effect of mixture flow rate on minimum wire ignition temperatures of hydrocarbon fuels in air at 150° C.

Fuel-air weight ratio, 0.4

test at a flow rate greater than 290 cc. per minute, the wire ignition temperature increased still further.

Relationship between Hot Surface Ignition Temperatures and Heat Source Dimensions. According to thermal theory, the ignition of a combustible mixture by a heated surface is governed by the rate of heat release from chemical reaction and by the rate of heat loss from the system. Furthermore, ignition should occur at a point in the mixture where the temperature is greatest. In AIT experiments, the gaseous mixture and the walls of the heated vessel are ordinarily at a uniform temperature; therefore, ignition should occur in the center of the vessel where heat reaction losses are minimum. However, in wire ignition temperature experiments, the temperature of the wire is usually much greater than that of the confining vessel and the combustible mixture not in contact with the heated surface. In such cases, ignition should take place at or close to the heated surface, as was observed in the present work.

Motion picture records in Figure 6 show the ignition and subsequent development of flame in two identical wire ignition experiments with an octane vapor-air mixture at 150° C. and a flow rate of 290 cc. per minute (NTP); a Nichrome wire of 0.13 cm. radius at a temperature of 1040° C. was used in each case. The ignitions occurred close to the downstream surface of the heated wire although the initial kernel of flame that developed at ignition is somewhat obscured in the reproduced pictures. The flame during the early stages was nearly spherical in both runs but proceeded at a higher rate in run 2. Flame speeds measured about 150 cm. per second during the early stages (0 to 15 msec.) and 50 cm. per second subsequently, until the flame front became ill-defined because of increasing heat losses. Also, little evidence of exothermic reaction prior to ignition was evident from temperature measurements made in these experiments. In contrast, the wire ignition of methane-air mixtures is reported by Ashman and Buchler (*2*) to display measurable preignition reaction; the higher temperatures (> 1470° C.) required with methane-air mixtures may account for the different ignition behavior displayed by octane and methane. The ignitions in both instances occurred at about the same point along the wire surface. This behavior could be expected if a wire has an irregular or contaminated surface at some point and could explain some of the inconsistencies which were found in the data reported here.

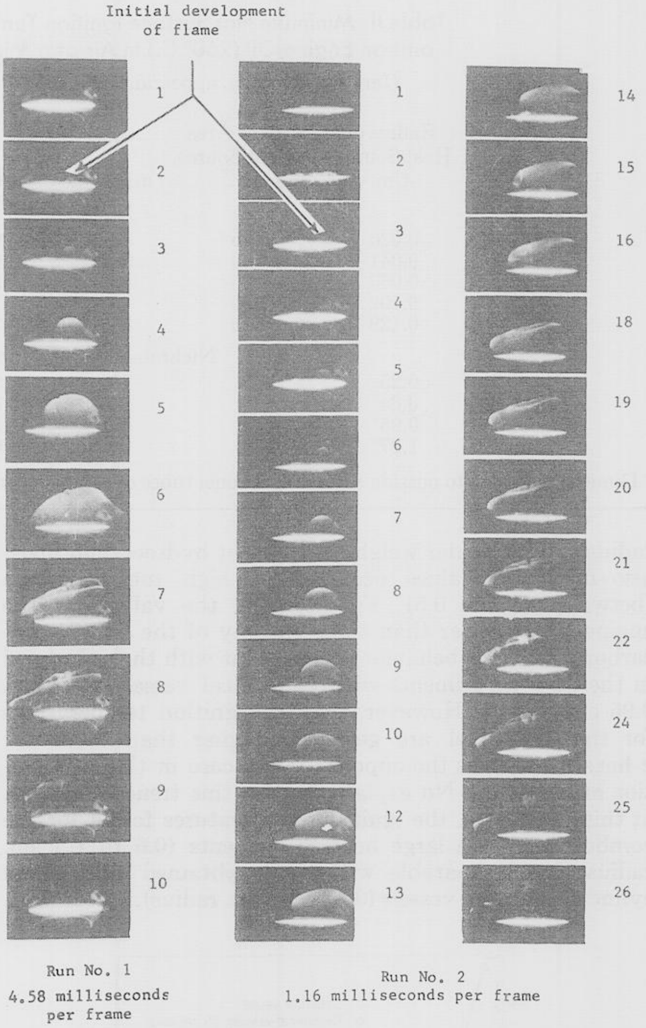

Figure 6. Motion picture records from two experiments showing the ignition of octane vapor-air mixtures with a heated Nichrome wire (5-cm. long and 0.13-cm. radius) at 1040° C.

Mixture flow rate, 290 cc. per min. (NTP); fuel air-weight ratio, 0.42 scale, 1 cm. = 3.1 cms.

For the case of thermal ignitions in heated vessels, the relationship between the ignition temperature, T, and the radius of the vessel, r, may be defined by the expression derived by Frank-Kamenetskii (*4*); the existence of a stationary temperature distribution and ignition in the center of the vessel, was assumed. For a cylindrical vessel, this expression is:

$$r = \left[\frac{2\lambda}{QE}\,\frac{RT^2}{Ze^{-E/RT}}\right]^{1/2} \qquad (1)$$

where Q is the heat of reaction of the combustible mixture with thermal conductivity λ, R is the universal gas constant, E is the activation energy, and Z is a rate collision factor. Equation 1 is applicable primarily to ignitions in small vessels and at low pressures where convective heat transfer may be neglected. Furthermore, it is similar to the expression derived by Semenov (*15*) for thermal ignition by heated wires. For this case, ignition is assumed to occur in a thin boundary layer near the wire surface, and the resultant equation is:

$$r \ln\frac{r'}{r} = \left[\frac{\lambda E}{2Q}\,\frac{(T-T_0)^2}{RT^2Ze^{-E/RT}}\right]^{1/2} \qquad (2)$$

where r is the radius of the wire, r' is the radius of the confining vessel ($r' \gg r$), and T_0 is the temperature of the vessel. In both cases, the extent of the preignition reaction is assumed to be small. The present experiments were consistent in this respect because little evidence of reaction prior to ignition was apparent from temperature measurements made to follow the wire ignitions and because the depletion of reactants would be small considering the high concentration of fuel required to obtain the minimum ignition temperatures. The extent of reaction prior to the autoignition of JP-6 fuel vapor-air mixtures has also been shown to be negligible (*7*).

The above expressions indicate that, as a first approximation, a plot of ln r *vs.* $1/T$ should be linear over a limited range of temperatures and heat source dimensions; a significant change in the reaction and heat transfer modes can be expected to be limiting factors. Figure 7*A* shows such a semilog plot of the ignition temperature data obtained under static conditions with heated cylindrical vessels and under flow conditions with wires and rods (or tubes). The wire and rod ignition temperature data for each combustible tend to display a linear relationship between $1/T$ and ln r but do not correlate with the vessel AIT data. The slopes of the straight lines drawn to represent the wire and rod ignition data for the hydrocarbon fuels do not vary significantly. Therefore, the following expression may be used to describe the approximate variation of these hot surface

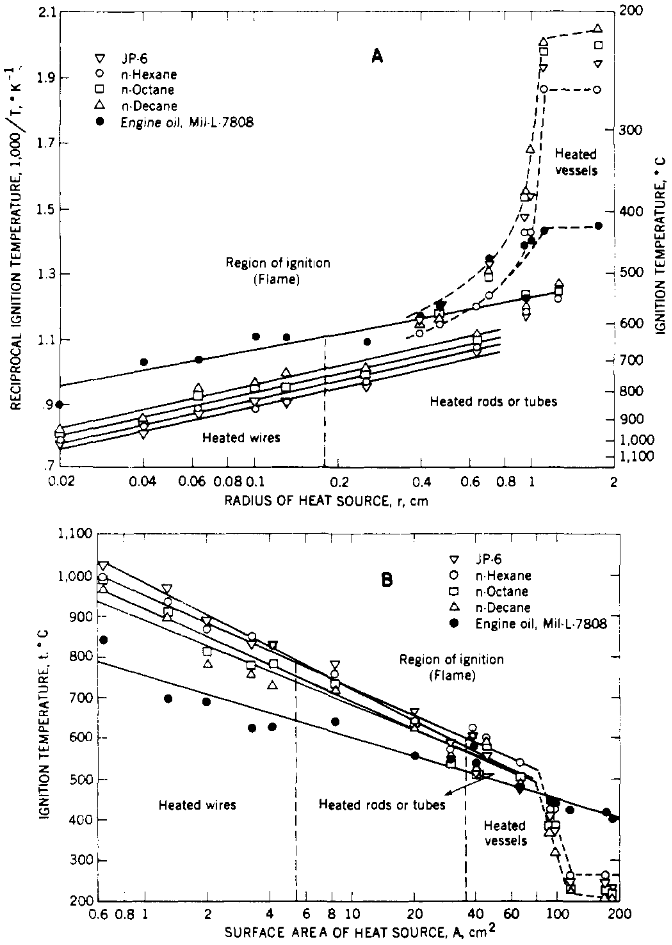

Figure 7. Hot surface ignition temperature as a function of (A) the heat source radius and (B) the heat source surface area for various hydrocarbon fuels and an engine oil in air

ignition temperatures (T, °K.) with the radius (r) of the heat source between 0.02 and 0.7 cm.:

$$\ln r = \frac{12{,}000}{T} - k \tag{3}$$

where k is 12.9 for JP-6 and n-hexane, 13.5 for n-octane, and 13.7 for n-decane. Similarly, for the engine oil, the following equation is applicable for r values between 0.02 and 1.3 cm.:

$$\ln r = \frac{14{,}000}{T} - 17.7 \tag{4}$$

For heat sources greater than about 0.7 cm. radius, the wire ignition temperatures for the fuels and the AIT's for the fuels and engine oil decrease sharply. Moreover, the above correlations for each combustible would not change significantly if less simplified forms of Equations 1 and 2 are fitted to the data—for example, plots of $\ln r/T$ and $\ln rT/(T - T_0)$ *vs.* $1/T$ for the heated vessel and wire ignition data, respectively, will give essentially the same slopes as shown in Figure 7*A*. Although the temperature coefficients in Equations 3 and 4 are characteristic of those expected for the high temperature oxidation of these hydrocarbon combustibles, an interpretation in terms of activation energy is not warranted because of approximation limitations and because of lack of corresponding kinetics data.

To some extent, the lack of a complete correlation of the hot surface ignition temperatures over the full range of heat source dimensions may be explained by the fact that the lengths of the cylindrical vessels (15 cm.) and those of the wires and rods (5 cm.) were not the same. Therefore, the correlation should improve, as was found here, by plotting the data as a function of the surface area of the heat source; Figure 7*B* shows a semilog plot of the ignition temperature against the surface area of the heat source. Here at least the AIT data for small vessels, those equal or less than about 0.7 cm. radius and 70 cm.^{2} surface area, are consistent with the wire and rod (or tube) ignition temperature results. Also, for the engine oil, the variation of ignition temperature is approximately linear over the entire range of surface areas investigated. The straight regression lines drawn to fit the data in this figure were determined by the method of least squares and are given below:

n-Hexane $\quad t = 951 - 98.5 \ln A;\ 0.6 < A < 70;\ S_{y/x} = 24 \quad (5)$

n-Octane $\quad t = 921 - 96 \ln A;\ 0.6 < A < 70;\ S_{y/x} = 31 \quad (6)$

n-Decane $\quad t = 893 - 89.5 \ln A;\ 0.6 < A < 70;\ S_{y/x} = 34 \quad (7)$

JP-6 $\quad t = 985 - 112 \ln A;\ 0.6 < A < 70;\ S_{y/x} = 20 \quad (8)$

Engine oil $\quad t = 752 - 64 \ln A;\ 0.6 < A < 190;\ S_{y/x} = 36 \quad (9)$

where t is the ignition temperature in ° C., and A is the surface area of the heat source in square centimeters; $S_{y/x}$ is a measure of the scatter in the vertical direction about the regression line. Most of the ignition temperature values fall within $\pm S_{y/x}$.

It is not altogether surprising that the wire ignition and autoignition temperatures for the engine oil correlated over the entire range of heat source surface areas, since relatively high temperatures (> 400° C.) are required for its autoignition even in large heated vessels. Therefore, the oxidation reactions controlling its ignition are of the high temperature type and apparently do not change significantly with increasing temperature, as evidenced by the linear plot obtained for the oil data in Figure 7*B*. Setchkin's data (*14*) for such high AIT fuels as benzene and toluene also correlate well over a large range of vessel dimensions (*7*).

In comparison, the vessel ignition temperature data given here for the hydrocarbon fuels extend down to as low as about 200° C. Furthermore, the reaction kinetics change abruptly to those of a less temperature-sensitive process as the temperature required for ignition is increased from about 250° ($A \cong 115$ cm.^{2}) to 500° C. ($A \cong 70$ cm.^{2}). This behavior is consistent with the ignition delay–temperature dependency which was previously reported for the autoignition of the JP-6 fuel with quiescent and flowing air mixtures (*8*); a number of hydrocarbon fuels tend to display similar autoignition behavior (*3, 8, 13*). For JP-6, the temperature coefficient describing the variation of ignition temperature with vessel radius (as in Equation 3) is approximately 2000 in the above transition region; this value is in agreement with that found at comparable temperature conditions from ignition delay measurements. Obviously, heat losses to the vessel walls were much greater for these ignitions than for those obtained with heated wires above about 500° C. and with heated vessels below 250° C.

The expressions given above are primarily applicable to cylindrical heat sources and to stagnant or low velocity flow conditions where ignition delay is relatively long (> 1 second) and unimportant, and where the ignition criterion is the appearance of visible flame. Although data are available on the variation of the ignition temperatures of hydrocarbon fuels with high flow conditions (delays ≪ 1 second), additional information is needed on the effect of heat source geometry and other factors to make such expressions more useful. Furthermore, such data should be obtained with other high AIT fuels to determine whether their hot surface ignition temperatures correlate with heat source dimensions as well as those of MIL-L-7808 engine oil, benzene, and toluene. Present work by the authors employing various heat sources is directed to this effort—e.g., recent data indicate that hot gas ignition temperatures also may not be much greater than wire or autoignition temperatures when the heat source sizes are equivalent.

LITERATURE CITED

(1) Affens, W.A., Johnson, J.E., Carhart, H.W., J. CHEM. ENG. DATA 6, 613 (1961).
(2) Ashman, L.E., Buchler, A., *Combust. Flame* 5, No. 2 .113 (1961).
(3) Elliott, M.A., Hurn, R.W., Trimble, H.M., *Proc. Am. Petrol. Inst., Sect. III* 35, 361 (1955).
(4) Frank-Kamenetskii, D.A., "Diffusion and Heat Exchange in Chemical Kinetics," p. 209, Princeton Univ., Press, Princeton, N. J., 1955.
(5) Guest, P.G., *U. S. Bur. Mines Tech. Paper* **475**, 1930.
(6) Jackson, J.L., *Ind. Eng. Chem.* **43**, 2869 (1951).
(7) Kuchta, J.M., Bartkowiak, A., Zabetakis, M.G., *U. S. Bur. Mines Rept. Invest.*, to be published.
(8) Kuchta, J.M., Lambiris, S., Zabetakis, M.G., *U. S. Bur. Mines Rept. Invest.* **5992**, 1962.
(9) Kumagai, S., Kimura, I., *Symp. Combust., 6th, Yale Univ., 1956*, p. 554 (1957).
(10) Mullen, J.W., Fenn, J.B., Irby, M.R., *Symp. Combust. 3rd, Madison, Wis., 1948*, p. 317 (1949).
(11) Mullins, B.P., *AGARDograph* **4**, 117 pp. (1955).
(12) Paterson, S., *Phil. Mag.*, S7 **28**, 1 (1939); *Ibid.*, S7, **30**, 437 (1940).
(13) Salooja, K.C., *Combust. Flame* **5**, 243 (1961).
(14) Setchkin, N.P., *J. Res. Natl. Bur. Std., Res. Paper* **2516**, **53**, 49 (1954).
(15) Semenov, N.N., *Natl. Advisory Comm. Aeron. Tech. Memo* **1024**, Washington, D. C., p. 41, 1942.
(16) Silver, R.S., *Phil. Mag., S7*, **23**, 633 (1937).
(17) Zabetakis, M.G., Furno, A.L., Jones, G.W., *Ind. Eng. Chem.* **46**, 2173 (1954).

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Thermodynamics of Liquid Surfaces

Surface Tension of a Homologous Series of α,ω-Alkane Dinitrate Esters

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The influence of temperature and number of methylene groups on surface tension and density has been investigated in a study of the physical and chemical properties of nitrate esters. The esters investigated were the α,ω-dinitroxy compounds of ethane through decane. The densities and surface tensions were measured at several temperatures, and thermodynamic quantities such as temperature coefficient and surface energy have been calculated.

THE POSSIBLE utilization of the dinitrate esters as fuel additives, propellants, and explosives indicates the value of data concerning their thermodynamic properties. Because of the lack of experimental data, it has been necessary to resort to estimations to obtain certain information involving these dinitrate esters. This investigation was undertaken to study the influence of the nitrate ester groups and the number of carbon atoms in the molecule on the surface tension.

EXPERIMENTAL

Materials. The α,ω-dinitroxy alkanes from ethane through decane were prepared by nitration of the corresponding diols (2). The esters were isolated by means of a Hickman Still, redistilled (under vacuum) and run through a Beckman Megachrom (20% paraplex on 40- to 60-mesh chromosorb W). The purity of the compound was better than 99%. No change in surface tension was measured between the twice distilled samples and those additionally run through the megachrom. Also no changes in the IR spectrophotometer curves were detected. Any remaining impurity in the nitrate esters will most likely come from the starting material, the diols. To study the effect of impurity on surface tension, trimethylene glycol was gradually added to a triply distilled propane dinitrate ester sample, and the surface tensions were measured. An addition of 1% trimethylene glycol caused a change in surface tension of approximately −0.14 dyne per cm.

Procedure. The densities were measured in a 1-ml. pycnometer which was calibrated at 25° C. Correction was applied for the variation of the pycnometer volume with the temperature (7). Surface tensions were measured by the maximum bubble pressure method using a Cassel surface tensiometer from the National Instrument Co. (*3, 6*). The apparatus, which is simple in operation, consists essentially of a thick-walled glass nozzle mounted in vertical position and a screw-operated piston to apply pressure. The glass nozzle has a conical-shaped aperture in the top, with the smallest diameter in the center of the nozzle tip. The exterior surface of the nozzle is flat and polished. The maximum pressure inside the bubble formed at the orifice is recorded by a manometer. Figure 1

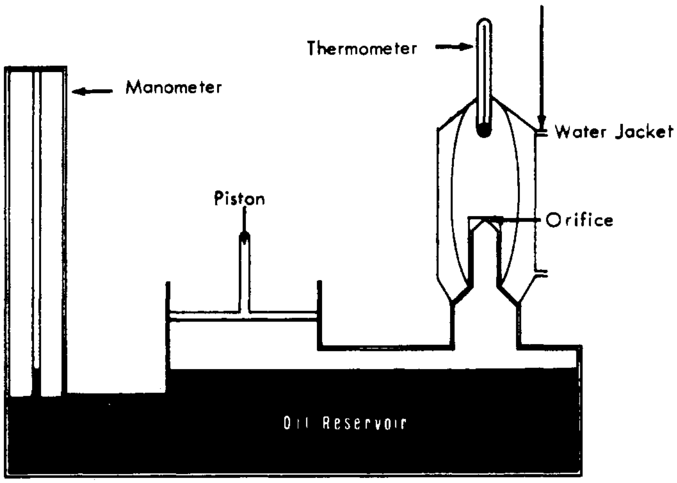

Figure 1. Schematic diagram of Cassel surface tensiometer