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Special Technical Report No. 8

IGNITION AND COMBUSTION OF SINGLE DROPLETS

Prepared for:

COMMANDING OFFICER
EDGEWOOD ARSENAL, MARYLAND 21010

ATTN: MR. DONALD E. BUCK
CONTRACT PROJECT OFFICER
DISSEMINATION RESEARCH DEPARTMENT
PHYSICAL RESEARCH LABORATORY

CONTRACT DA-18-035-AMC-122(A)

STANFORD RESEARCH INSTITUTE

MENLO PARK, CALIFORNIA

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CONTRACT DA-18-035-AMC-122(A)

By: BERNARD J. WOOD AND WILLIS A. ROSSER, JR.

SRI Project PAU-4900

Approved: C. J. COOK, EXECUTIVE DIRECTOR
CHEMICAL, THEORETICAL, AND APPLIED PHYSICS

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FOREWORD

The work reported herein was authorized under Task 1B522301A08101, Dissemination Investigations of Liquid and Solid Agents (U). The work was started in April 1964 and completed in December 1966.

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Acknowledgment

Much of the experimental work in this program was carried out by Mr. Richard C. Smith. Dr. R. L. Peskin and Mr. P. S. Yeh, of Rutgers University, very kindly carried out some theoretical calculations and were most helpful in discussing the interpretation of the experimental results.

DIGEST

By means of photographic techniques, the size histories, ignition lags, and loci of ignition of small (100-300 microns diameter), single, freely falling fuel droplets suddenly exposed to a hot, oxidizing atmosphere in a furnace were determined as a function of initial droplet size, oxidizer temperature, fuel composition, and droplet spacing. The results show that ignition lag depends significantly on the temperature of the atmosphere, on the droplet-droplet spacing, and on the chemical nature of the fuel, but it appears to be only weakly affected by the oxygen concentration in the oxidizer. The ignition lag seem to be independent of the initial droplet size if the droplets are large enough to ignite at all. This characteristic insures that droplets with initial diameters smaller than a characteristic value will not ignite during their lifetimes. In spite of the complexity of the ignition process, the experimental results correlate satisfactorily with theoretical models that seem to represent a reasonable approximation to the physical situation of a spontaneously igniting fuel droplet.

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I INTRODUCTION

The purpose of this study was to define the limits of one process that may be involved in the degradation of explosively disseminated agents. Specifically, this report deals with the problem of spontaneous aerosol droplet ignition which has often been suggested as one facet of aerosol degradation or "flashing." Several parameters and relationships are pertinent in this regard:

1. Droplet diameters and temperatures required for spontaneous ignition;
2. Time lags to be expected between exposure of droplets to hot oxidizing atmosphere and ignition;
3. Effect of droplet velocity on ignition characteristics;
4. Effect of oxidizer composition on ignition characteristics;
5. Effect of droplet spacing on ignition characteristics; and
6. The locus of ignition relative to the liquid droplet.

Unlike a premixed, combustible, gaseous system, a combustible aerosol is not uniform in composition. Fuel is present as discrete liquid sources. Usually a wide range of drop sizes is involved and the drops are moving at various speeds relative to the surrounding gas. The lack of microscopic uniformity causes irregularities in the propagation of a flame through a combustible aerosol. The size and shape of the combustion region is poorly defined and the rate of flame propagation may vary erratically with time. Visual observation of such a flame reveals that many of the droplets burn as discrete individuals and indicates that an accurate description of single droplet combustion will be required for analysis of aerosol combustion.

The rate of flame propagation is only one aspect of aerosol combustion. Others of interest include flammability, quenching, and ignitability. All three involve attainment of some critical condition in which a steady state balance between the rate of heat release by chemical

reaction and the rate of heat loss is not possible. Necessarily, the system must then undergo a transition from one steady state to another. In particular, autoignition is the spontaneous transition from a state in which the rate of chemical reaction is small to one in which the rate is large and is associated with a visible flame. Quenching is the reverse transition. The tendency of an aerosol to undergo such transitions will certainly be affected by the tendency of individual droplets themselves to ignite or to be quenched. As in the case of steady state flame propagation, an understanding of single droplet behavior will contribute to an understanding of aerosol behavior.

Extensive studies[1,2] of the combustion characteristics of single droplets have contributed to a satisfactory analytical theory of steady state droplet burning. The ignition process, however, is less perfectly understood. Consequently, the object of this program was to elucidate the mechanism of spontaneous ignition of a liquid droplet in terms of a mathematically tractable yet physically realistic model.

II EXPERIMENTAL STUDIES

A. Approach

To understand the process of droplet ignition, certain parameters and their mutual dependence must be determined quantitatively. For a specific fuel of known thermodynamic and transport properties and a specific oxidizer temperature, we must know the rate of vaporization preceding ignition, the size of the droplet at ignition, and the duration of the ignition lag. Experiments on these variables have been carried out by many investigators using a variety of techniques.[1] In general, however, those who were able to observe the ignition behavior of individual droplets employed large drops (diameter > 1000 μ) suspended on fibers; those who employed small, unsupported droplets depended on average mass or diameter changes and time extrapolations to obtain vaporization rates and ignition lags.

Our approach was to attempt direct and simultaneous measurement of the rate of vaporization, the diameter, and the ignition lag of small ($D \sim 100\ \mu$), freely falling droplets suddenly exposed to a hot oxidizing atmosphere, and to determine the effect on these parameters of droplet velocity relative to the oxidizer, droplet initial diameter, and oxidizer composition and temperature.

B. Techniques

1. Measurement of Pre-Ignition and Post-Ignition Droplet Vaporization Rates

A photographic technique employing dark-field illumination was adapted to follow a liquid-fuel droplet along a free-fall trajectory in a heated furnace. The device, shown schematically in Fig. 1, consisted essentially of a camera, with a sufficiently long bellows to give 10 X magnification looking through a furnace equipped with quartz windows into a dark-field condenser. The condenser collected light from a

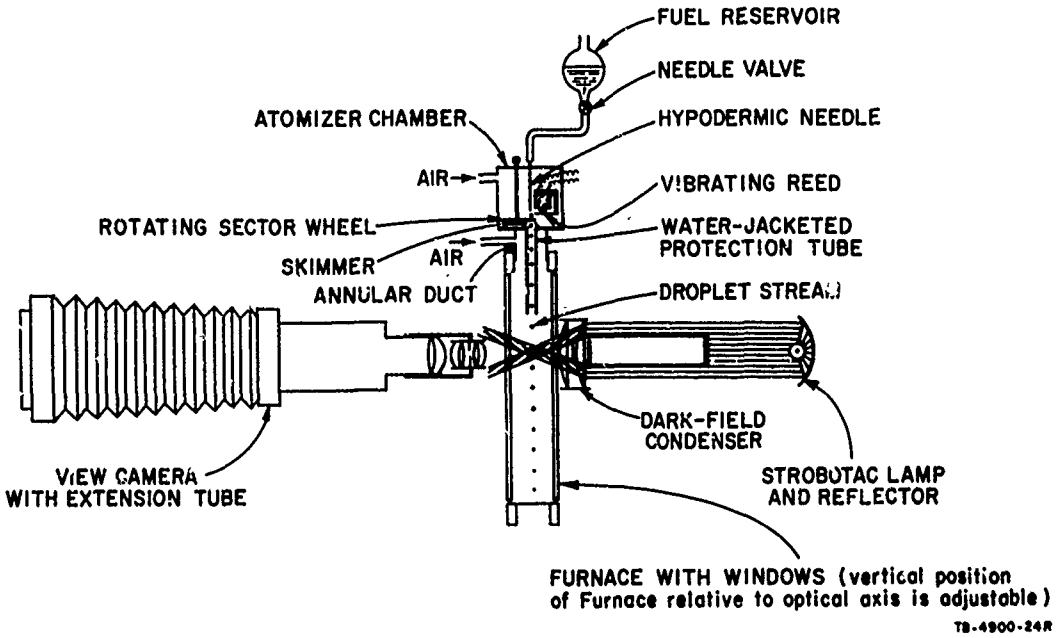

FIG. 1 SCHEMATIC DIAGRAM OF APPARATUS WITH DARK-FIELD PHOTO-OPTICAL ACCESSORY

Strobotac* and focused it in a hollow cone at a point near the vertical axis of the furnace. Light diverging from this focal point fell outside the aperture of the camera lens, unless a spherical transparent droplet was situated in the cone. In that case, the droplet acted as a secondary lens which focused an image of the condenser into the field of view of the camera. The film recorded a bright ring with a diameter proportional to the focal length (and therefore the diameter) of the droplet. The constant of proportionality was determined empirically using glass spheres of known size fused on the ends of fine fibers in addition to freely falling liquid droplets sized by a standard replication technique.[3] A typical photograph is shown in Fig. 2.

A monodisperse stream of droplets was produced by means of a resonant reed atomizer[4] driven at 60 cycles/sec. This device was equipped with a rotating sector wheel which could interrupt the droplet stream. Thus, either a steady stream of droplets following each other at a rate

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* General Radio Corporation, Cambridge, Mass.; Model 1531-A.

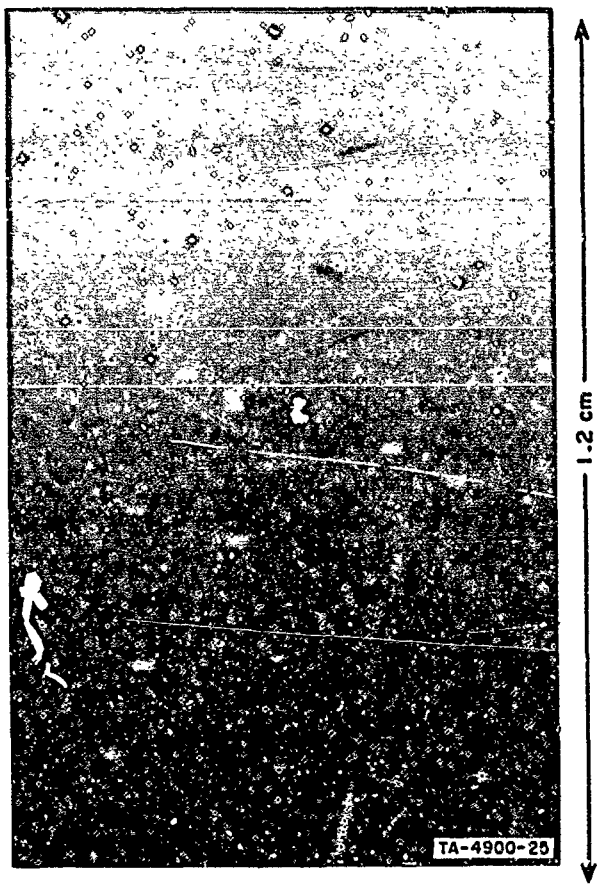


FIG. 2 TYPICAL PHOTOGRAPH OF DROPLETS.
Droplet diameter 160μ. Droplet velocity 85-105 cm/sec. This film was exposed for approximately 20 sec with the strobe flashing at a rate of 400 sec^{-1}. Hence it represents about 8000 exposures. Most of the droplets are out of focus, but many of the images are distinct multiple exposures of the same droplet which can be identified by the recurring group patterns.

of 60 droplets/sec, groups of a few droplets spaced at about 1-sec intervals, or a succession of separated single droplets could be obtained from the atomizer. In every case the droplets fell through a water-cooled tube extending into the center of the furnace along its axis. When the droplets emerged from this tube, they were suddenly exposed to a high temperature environment. Air was forced through the water-cooled tube and the furnace from top to bottom at a total volumetric flow rate of 10 liters/min. This resulted in a high linear air velocity in the

droplet protection tube which diminished to about 5 cm/sec in the body of the furnace, thus permitting a reasonably uniform (±5%) axial temperature profile to be maintained.

The field of view of the camera encompassed a length of 1.2 cm; hence, in many cases, only a fraction of the lifetime trajectory of a droplet could be recorded on one photograph. Fractional trajectories of various droplets were obtained by raising or lowering the furnace with respect to the camera. Droplet diameters down to 50 μ were easily resolved on Polaroid Land 57 (3000-speed) film, using a simple optical comparator to make the measurement.

The Strobotac was ordinarily set to flash at a rate of 400 sec^{-1}. With such illumination, each droplet falling through the field of view of the camera would be recorded on the film as a series of images separated in time by 2.5 msec. Hence, the rate of change of diameter of the droplet with time (and thus its rate of vaporization) could be derived directly from the photograph. Light emitted by burning droplets was too dim to record on the photographs. Whether ignition occurred was determined from visual inspection of the droplet stream in the furnace.

2. Direct Measurement of Ignition Lag

In order to measure directly the time interval between the arrival of the droplet in the hot furnace and the appearance of a flame, i.e., the ignition lag, a modified dark-field optical system was devised. The droplet stream was illuminated obliquely from the rear by the collimated light beam of the Strobotac. The light was directed at an angle such that the primary beam was outside the field of view of the camera. With this arrangement, light scattered by the droplets in addition to light emitted by flames was recorded by the camera. The images on the film indicated the time-position history of the falling droplet but not the time-diameter history. Hence, in conjunction with these measurements, the initial diameters of the droplets were determined by a standard replication technique.[3] Since the appearance of the flame could be seen in the photograph (Fig. 3), the ignition lag could be measured directly.

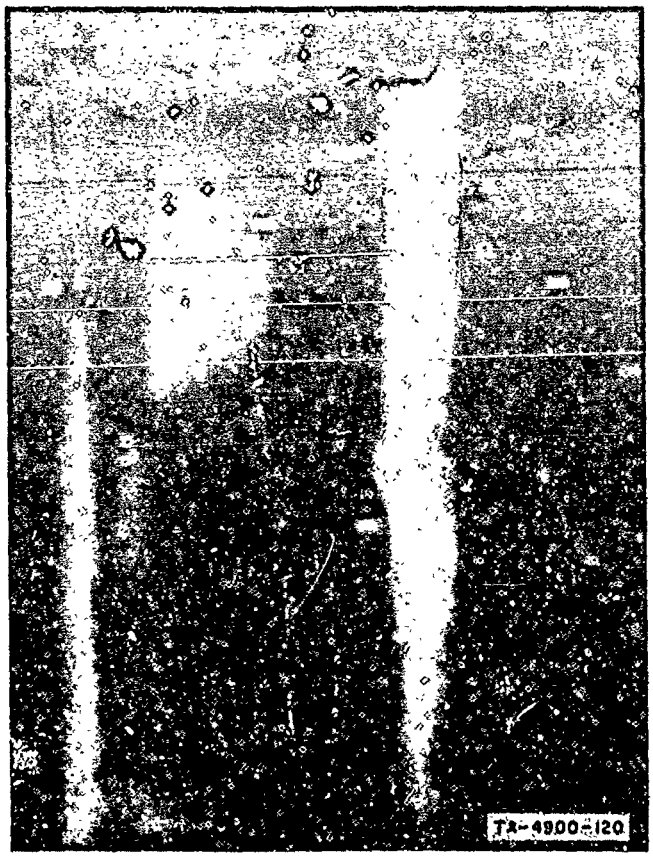


FIG. 3 TYPICAL PHOTOGRAPH OF IGNITING DROPLETS. Droplet images are separated by 2.5-msec time intervals. Furnace temperature is 630°C; initial diameter of droplets is 143μ.

3. Variation of Droplet Velocity Relative to Air

In the size range under investigation the droplet velocity within the furnace depends partly on the flow conditions within the entry tube. A substantial effort was expended to vary droplet velocities systematically by accelerating the entry tube air stream through a nozzle. It was hoped that droplets carried in this air stream would gain sufficient momentum to sustain their enhanced velocity for a significant length of time after entering the virtually stagnant atmosphere in the furnace. All sizes of droplets, however, attained a settling velocity relative to

the furnace air that was nearly independent of the nozzle air stream velocity. Hence no quantitative measurement of the effect of droplet velocity on ignition lag or ignitability could be made.

4. Schlieren Photography

Surrounding a burning droplet which is moving with respect to its gaseous environment is a contact surface located at some distance from the droplet. Such a contact surface is defined by the streamlines that separate the oxidizing gas from the combustion products emerging from the enclosed flame.[2] Since the combustion products are likely to be considerably hotter than the oxidizing gas, and since mass transfer across the contact surface can occur only by diffusion, a sharp density gradient will be associated with the contact surface. Such density gradients can be visualized by means of schlieren photography. Hence, a schlieren optical system was erected with the expectation that the appearance and location of a flame and an associated contact surface around a droplet could be discerned at the moment of ignition. The apparatus (Fig. 4) was modeled after the design of D. A. Senior[5] to give a schlieren image magnification of 8 to 10X.

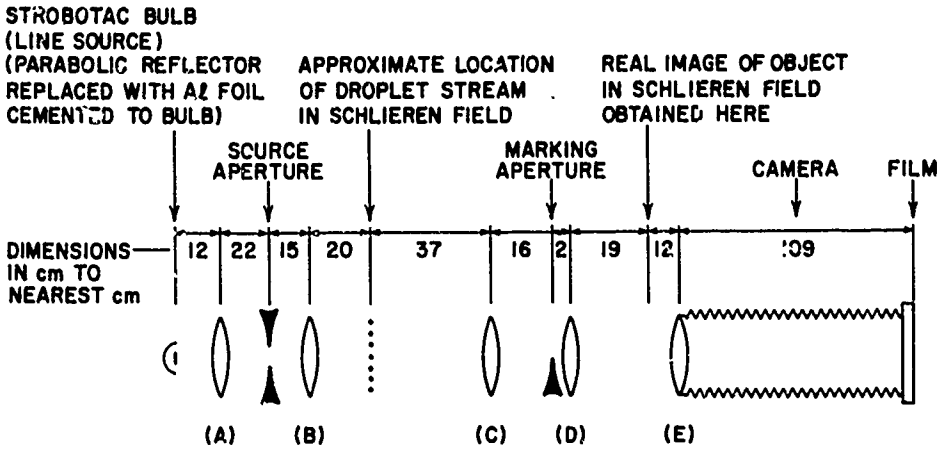
For still photographs, the Strobotac was flashed by means of the synchronizing device in the camera shutter. For motion pictures, the view camera was replaced with a Hycam high-speed motion picture camera. This camera utilizes a rotating prism with a sector-wheel shutter to control exposure, and is equipped with a pulse generating device driven by the shutter. By means of this device, the Strobotac flash was synchronized with the shutter at speeds up to 500 frames per second.

C. Results

1. Vaporization Rates

Spherical liquid drops have been observed[1] to vaporize in accordance with a diameter-squared law

$$D^2 = D_o^2 - \epsilon t \qquad (1)$$



LENS	FOCAL LENGTH (mm)	DIAMETER (mm)	TYPE
(A)	75	46	ACHROMAT
(B)	150	48	ACHROMAT
(C)	160	65	ACHROMAT
(D)	185	51	ACHROMAT
(E) (STILLS)	114	25 (f. 4.5)	RAPTAR ANASTIGMAT WITH RAPAX SHUTTER
(E) (MOVIES)	200 203	70 58 (f. 3.5)	ACHROMAT IN FRONT OF TAKUMAR ANASTIGMAT } COMPOUND LENS

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FIG. 4 SCHLIEREN OPTICS (not drawn to scale)

where D_o is the initial drop diameter and the slope of the plot of diameter squared, D^2, against time, t, is termed the evaporation constant ϵ. Our results, exemplified in Fig. 5, indicate that this law is followed by hexadecane droplets in the size range and under the conditions employed in our experiments. Our results for hexadecane droplets are summarized in Table I.

Less extensive measurements of the vaporization rates of aniline droplets were also carried out. At an air temperature of 600°C, droplets of this fuel exhibited an evaporation constant $\epsilon = 4 \pm 1 \times 10^{-3}$ cm^2/sec. This is somewhat lower than the value obtained for hexadecane under similar conditions (Table I), as one would expect from consideration of the stationary state conductive heat-transfer model of a vaporizing droplet.[6]

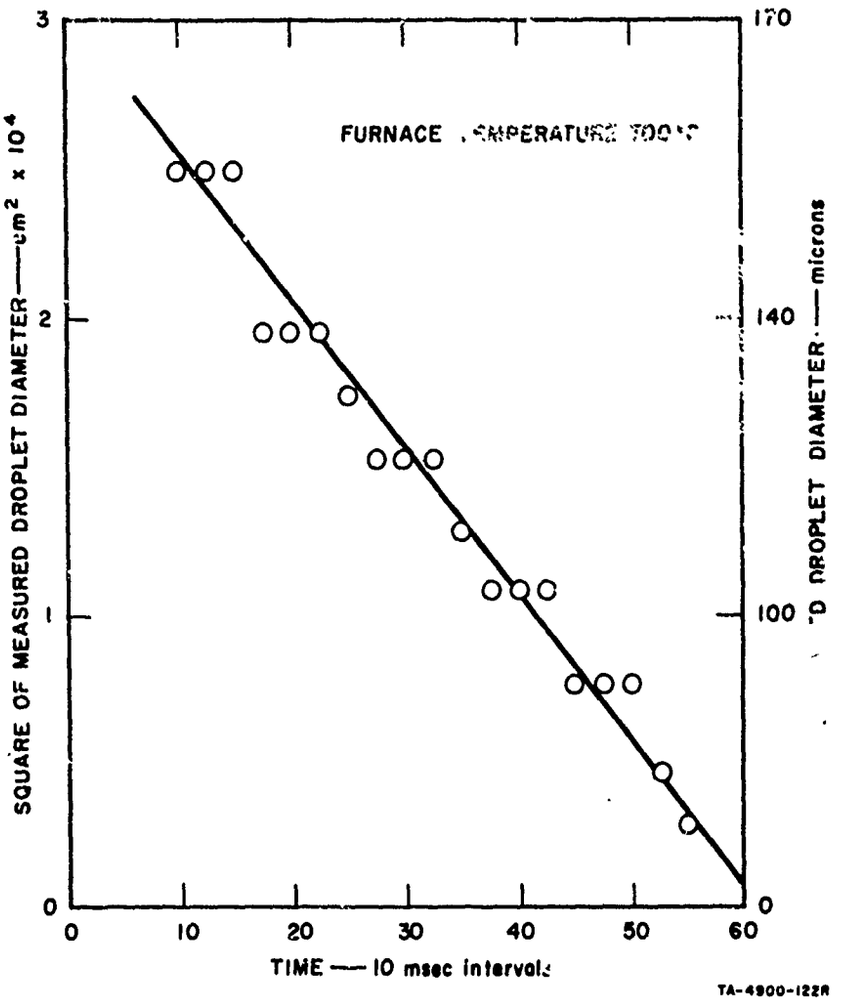


FIG. 5 TYPICAL EXPERIMENTAL TIME-DIAMETER HISTORY OF VAPORIZING HEXADECANE DROPLET. Furnace temperature 700°C.

Table I

MEASURED EVAPORATION CONSTANTS OF HEXADECANE DROPLETS
(based on droplet diameter)

Furnace		Droplet Stream, drops/sec	Evap. Constant, ϵ (cm^2/sec) $\times 10^3$		Initial Droplet Diameter μ
Atmosphere	Temp., ^oC		Pre-ignition	Post ignition	
Air	830	3		9.5	173
		60		15.0	158
Air	750	3		6.3	173
					173
N_2	720		5.3		139
			5.3		
Air	750	60		11.7	196
Air	700	3	6.2	6.3	196
					189
Air	690	3	6.2		196
N_2	680		6.3		196

2. Characteristic Initial Droplet Diameter for Ignition

The results of earlier experiments in which 60-droplet/sec streams of fuel oil were directed into a hot oxidizing atmosphere indicated that a characteristic minimum size for ignition existed at each temperature and oxidizer composition. Droplets initially smaller than this size vaporized completely without the appearance of a flame, while those of larger size ignited and burned with a visible flame. This characteristic diameter decreased with increasing oxidizer temperature. Similar experiments with hexadecane demonstrated similar results, but when the droplet frequency in the stream was reduced first to groups of 3 or 4 drops at approximately 1-sec intervals and finally to isolated single droplets, significantly different results were obtained. The data for single droplets are shown in Fig. 6 and the effect of droplet-droplet proximity is illustrated in Fig. 7.

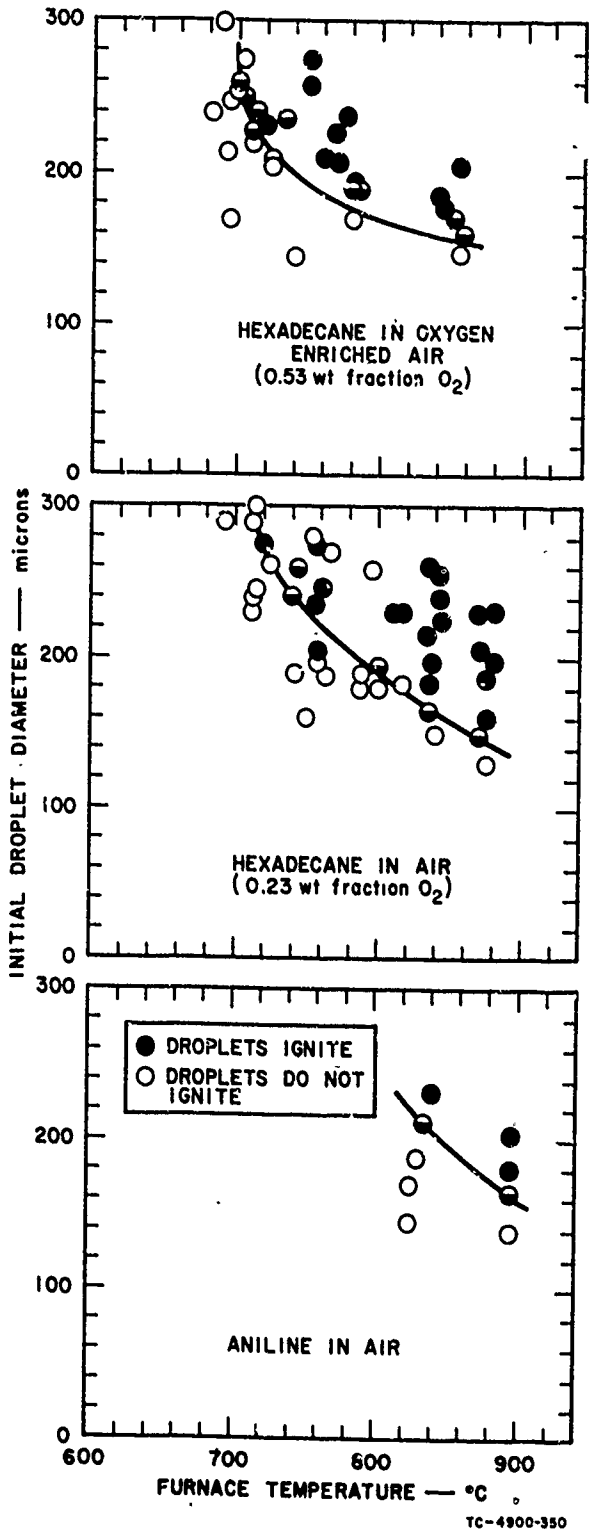


FIG. 6 CHARACTERISTIC IGNITION CURVES SHOWING RELATIONSHIP BETWEEN INITIAL DROPLET DIAMETER, OXIDIZER TEMPERATURE, AND IGNITABILITY. Droplet velocity (relative to air) is ~ 60cm/sec.

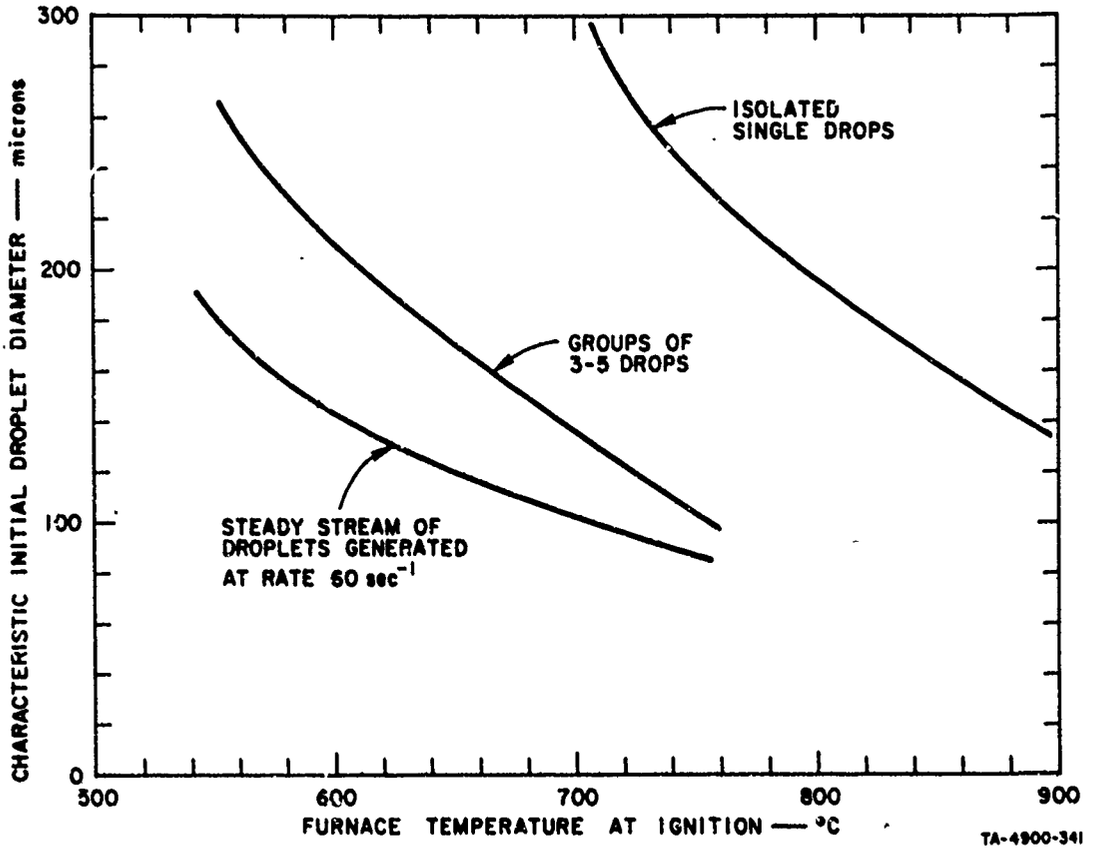


FIG. 7 CHARACTERISTIC IGNITION CURVES FOR HEXADECANE DROPLETS IN AIR

3. Ignition Lag

A substantial number of direct measurements of ignition lag were made on groups of 3-5 hexadecane droplets with initial diameters from 120 to 170 μ in the temperature range 590-740°C. The data indicate a small dependence on temperature but show no systematic dependence on initial diameter (open symbols in Fig. 8). Based on the observed logarithmic variation of ignition lag τ with temperature T,

$$\tau = A\, e^{+E/RT}, \qquad (2)$$

the droplets exhibit an apparent activation energy E for ignition of 13 kcal/mole.

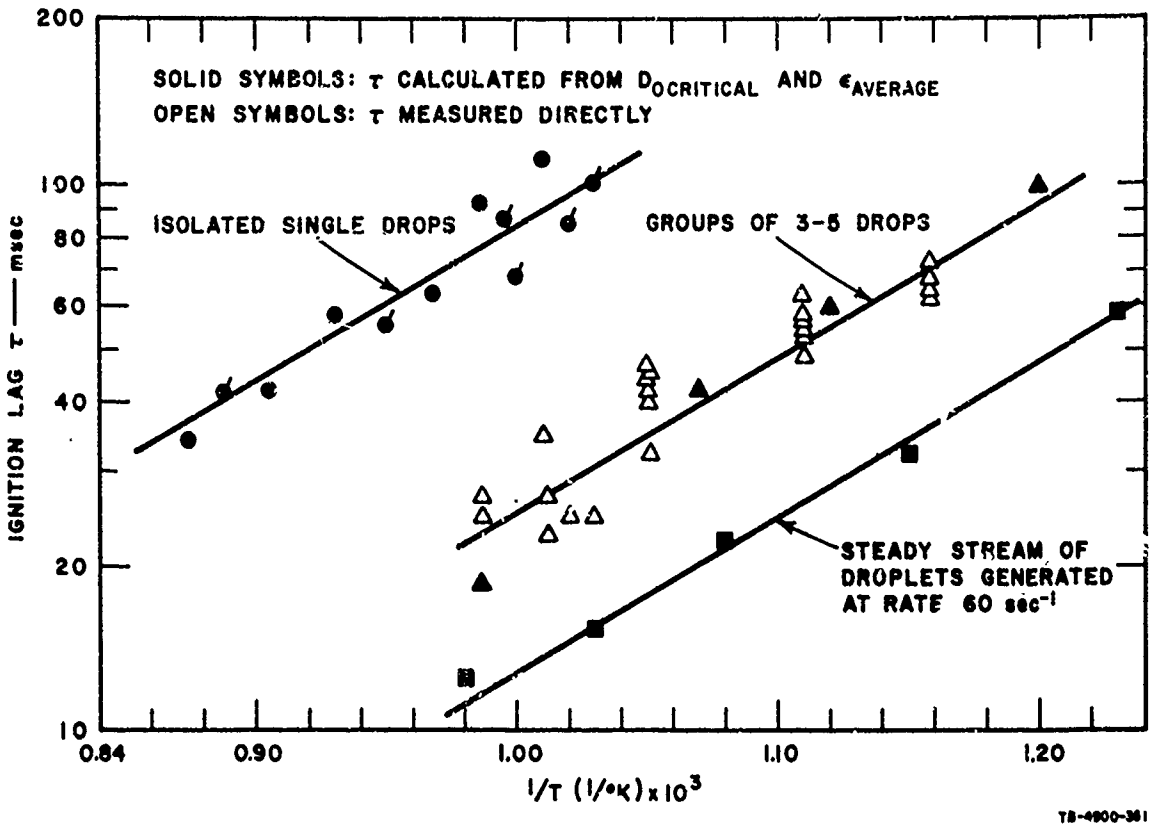


FIG. 8 IGNITION LAG OF HEXADECANE DROPLETS AS A FUNCTION OF OXIDIZER TEMPERATURE AND DROPLET-DROPLET PROXIMITY. (Oxidizer: air, except ✓ ; 0.53 wt. fraction oxygen.)

Ignition lag can also be determined indirectly from the measured characteristic diameters for ignition (Figs. 6 and 7) and the measured pre-ignition evaporation constants (Table I). When a droplet with an initial diameter equal to the characteristic diameter ignities, it does so in a flash. In this case the initial mass of liquid fuel has virtually completely vaporized before the critical condition for ignition is attained, and when ignition does occur at this moment, the liquid fuel which remains is sufficient to sustain only a brief flash of blue flame. The ignition lag τ is thus the time interval required for the droplet of this characteristic initial size D_o to be completely vaporized. In such a case, the droplet diameter at ignition, D, may be considered to be zero, and equation 1 becomes $D_o^2 = \epsilon\tau$. Thus, the ignition lag τ can be computed from the measured initial size of the droplet and its rate of evaporation (Table I).

On the basis of the measured characteristic diameters for ignition (Figs. 6 and 7) and the average vaporization rate (Table I), the values of ignition lag for those droplets which exhibited ignition just before completely evaporating were calculated and plotted with the direct ignition lag data (solid symbols in Fig. 8). Both sets of data are in agreement. Similar data for isolated single droplets and 60 drops/sec streams are also shown in Fig. 8.

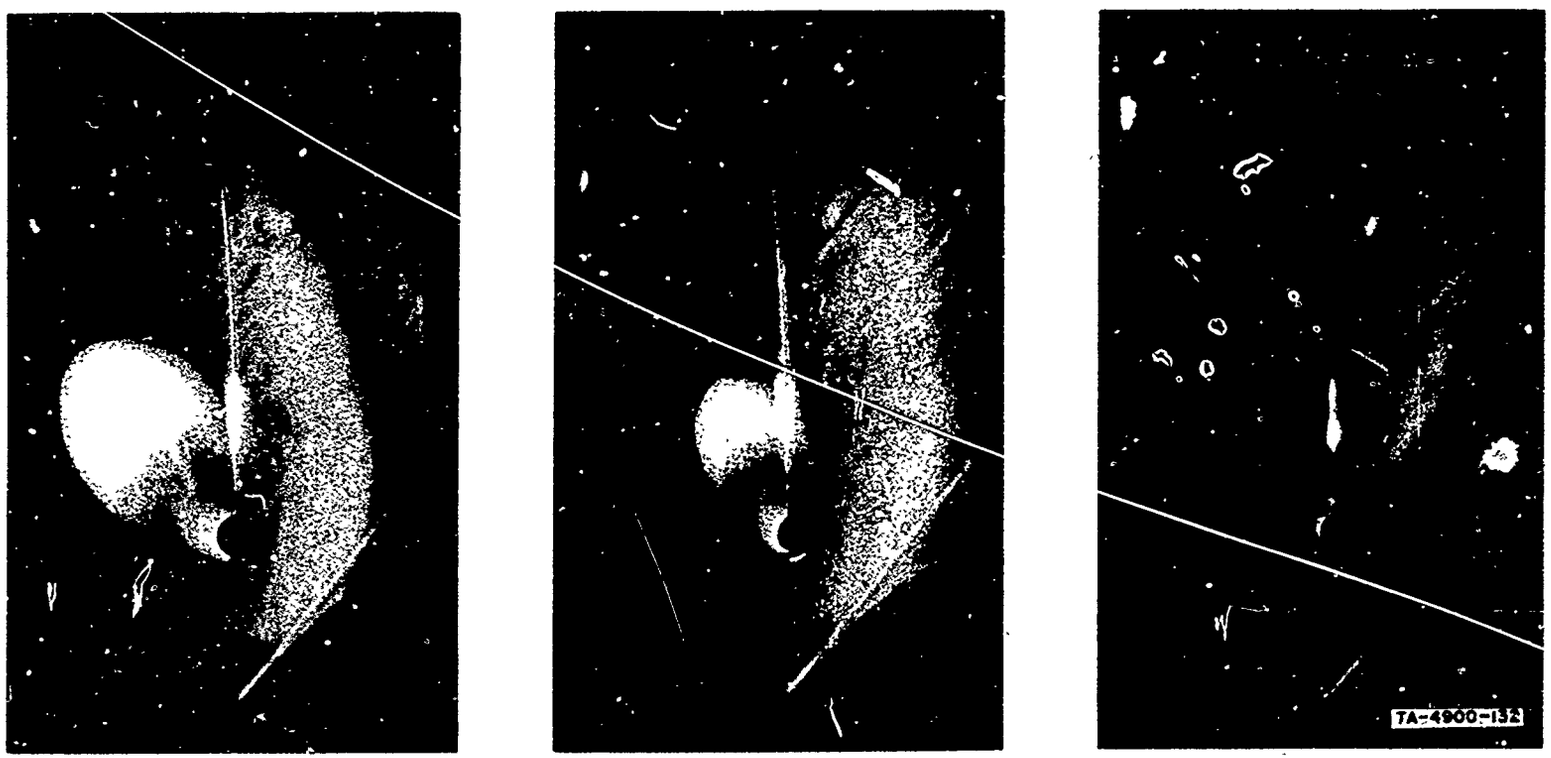
Ignition lags for single aniline droplets at two temperatures, 835 and 895°C, were also computed from the characteristic diameter for ignition (Fig. 6), and found to be 68 and 113 milliseconds, respectively.

4. The Locus of Ignition

The schlieren optical system was tested and calibrated using burning droplets suspended on the end of a fine quartz fiber. In a room-temperature air atmosphere, these droplets demonstrated a pronounced and easily identified contact surface on the schlieren photographs (Fig. 9). Note that in Fig. 9(c), just prior to extinction, the contact surface slips into the wake region of the droplet.

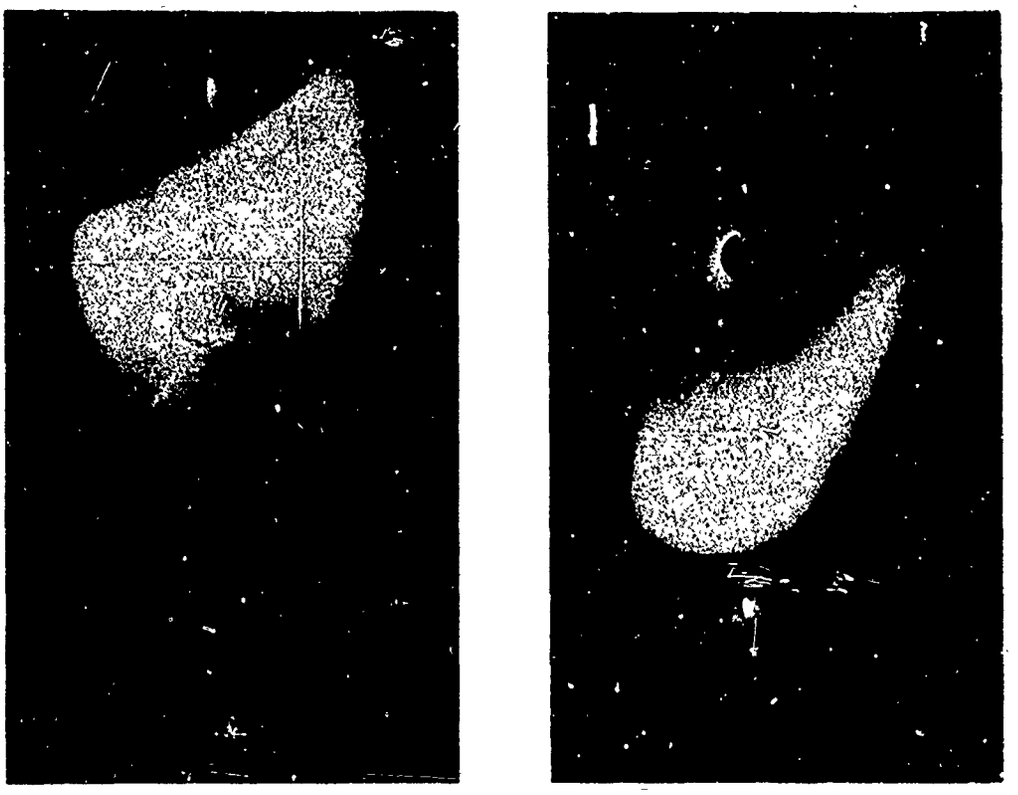
When the pendent drop is surrounded by a hot gaseous atmosphere, a contact surface is not visible (Fig. 10). This is also the case for the freely falling burning drops. The photos of the pendent drops, however, demonstrate the profound effect of gas-droplet relative velocity on the shape of the flame (Fig. 10).

By using the high-speed motion picture camera, it was possible to follow the disposition of a single droplet over a portion of its trajectory in the furnace. The camera was located so that the region where the droplet ignited was near the center of the field of view. A large number of droplets of hexadecane were photographed in this way. As with the still photographs of the freely falling droplets, neither a contact surface nor a flame boundary could be discerned on the films. However, a yellow region in the wake of a droplet showed up vividly. The appearance of such yellow flames seemed to be associated with the trajectories of two or more drops traveling close together. The motion pictures showed that the yellow incandescence invariably commenced in the wake of the droplets, pursued them, and sometimes overtook them. This suggests that ignition commences in the wake of the



(a) (b) (c)

FIG. 9 TYPICAL SCHLIEREN PHOTOGRAPHS OF PENDENT DROPLETS OF HEXADECANE
(Diameter of tip of supporting fiber ~ 250μ.) Ambient temperature = 50°C.



(a) (b)

FIG. 10 SCHLIEREN PHOTOGRAPHS OF PENDENT DROPLETS OF HEXADECANE IN FURNACE. Furnace temperature = 610°C. Downward air velocity in (a) = 27 cm/sec; in (b) = 54 cm/sec.

with the formation of a flame that propagates in the same direction as the droplet's motion, and possibly eventually envelops the droplet.

D. Discussion

1. Droplet Vaporization Rates

At furnace temperatures of 750°C and less, the observed rates of vaporization of single hexadecane droplets appear to be identical before and after ignition of the droplet (Table I). Yet, under identical conditions of oxidizer and temperature, droplets burning in a steady stream of 60 droplets/sec exhibit evaporation constants larger by about a factor of two than those observed for nonburning droplets. These latter results agree with earlier work[7,8] and with the theoretical model[6] of droplet combustion in which conductive heat transfer from the flame to the droplet governs the rate of vaporization of the liquid.

We conclude that in experiments in which the evaporation constant ϵ of a single droplet does not increase after ignition the flame is not thermally coupled to the evaporating droplet and does not supply the energy required for continued evaporation of the drop. Rather, the hot furnace atmosphere supplies the evaporation energy and the heat released by combustion is dissipated. It seems likely, especially in view of the schlieren photographs discussed below, that such an "uncoupled flame" is a flame in the wake of and at some distance from the droplet. Such wake flames which have been observed in extinction studies with large, stationary-state drops, have been interpreted in a similar way.[9]

In the case of a stream of droplets, combustion may begin in the wake of a single droplet but the resulting flame must then propagate throughout the "column" of vapor surrounding the stream of droplets and establish a localized high temperature region into which succeeding droplets fall and are ignited. Under these circumstances the droplet flame must enclose the droplet rather than be restricted to the wake region.

2. Ignition Lag and Associated Effects

Previous studies[1,7,10-13] of droplet ignition do not in themselves give the principal features of even a qualitative model for the process. They do suggest that the total ignition lag represents the time required to reach a critical state or size, that internal heating of the droplet is an important feature of the problem, and that not all droplets will reach the critical state during their evaporation lifetime.

One approach to an analytical model for an igniting droplet considers the energetic conditions which permit a steady state temperature distribution within a spherical shell of reactive vapor (Fig. 11). The inner boundary of the shell ($r = a$) represents the surface of the droplet, and the outer boundary ($r = b$) the contact surface between the reactive vapor and the oxidizer. This model is analogous to simpler systems of similar geometry, such as slabs[14] or spheres[15] of explosive solids, for which mathematically tractible solutions have been obtained. As the temperature of the outer boundary of such a system is raised, a critical condition will be approached in which the rate of heat loss from the reactive region is balanced by the rate of heat generation due to

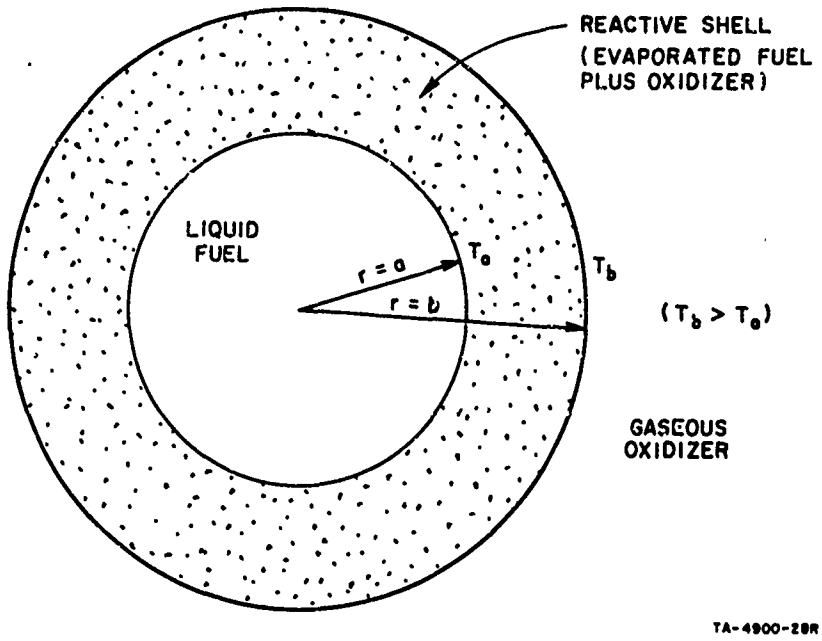


FIG. 11 A REACTIVE SPHERICAL SHELL

exothermic chemical reaction. This is a metastable situation, however, and and a slight increase in temperature will produce thermal run away (explosion or ignition). Likewise, in the absence of heat loss (an adiabatic system) such a mass of reactive material initially established at a fixed temperature T_b will ignite or explode in a time τ_a related to the rate of heat generation by chemical reaction. By analogy to the cited cases, critical conditions for droplet ignition will involve (1) the surface temperature of the droplet, (2) the ambient temperature, (3) the size of the droplet, (4) the velocity of the droplet relative to the ambient atmosphere, (5) the rate of evaporation, and (6) the kinetics of reaction between evaporated fuel and oxidizer.

The mathematical development of this model is discussed in detail in Special Technical Report No. 20 by W. A. Rosser, Jr., and Y. Rajapakse. Because of the mathematical complexity, the model deals only with the steady-state energetics of the situation, so it is capable of exhibiting the effects of reaction rate constants and activation energies on ignition, but it does not explicitly include the possibly important roles of fuel-oxidizer stoichiometry, ambient oxygen concentration, and the

time required for a super-critical system to ignite. Nevertheless, it is of interest to note that the observed contact surface dimensions of pendent drops taken from schlieren photographs are of the same order of magnitude as the critical dimensions of an igniting drop predicted by this model (Table II).

Table II

CRITICAL DIMENSIONS OF A BURNING DROPLET

Droplet Diameter (inner boundary, a) (microns)	Ratio of Outer to Inner Boundary, b/a		
	Experiment*	Theory	
		$\tau = 10^{-3}$ sec	$\tau = 10^{-2}$ sec
340	9.6	6.1	12.0
740	5.8	3.7	7.1

* Contact surface surrounding burning, pendent hexadecane droplet (cf. Fig. 9).

Recently, Peskin and Wise[16] and Peskin and Yeh[17] reported another theoretical approach to droplet ignition in which the effects of fuel-oxidizer stoichiometry and oxygen concentration in addition to reaction kinetics have been incorporated. Like the theory of Rosser and Rajapakse, discussed above, this model is based on a spherically symmetric droplet-oxidizer system (Fig. 11), but instead of a reactive shell of fuel vapor, it postulates a "modified flame surface." This is a hypothetical region in which chemical reaction occurs at a finite rate characteristic of some radial distribution of fuel and oxidizer. To make the model computationally feasible, the product of fuel and oxidizer concentrations are represented by a mathematical operator, a Dirac delta function, centered at the flame surface. Physically, this may be viewed as a limiting case of a class of finite flame thickness approximations in which the reaction region is compressed to one specific location with respect to the liquid drop surface. Based on this model, differential equations of continuity and energy conservation may be stated and solved within appropriate boundary conditions. The theory successfully accounts for the observed behavior of droplets in the evaporation limit (reaction rate $\rightarrow 0$) and

in the steady-state combustion limit (reaction rate $\rightarrow \infty$) where heat and mass transfer processes govern the rate of vaporization of a droplet. Furthermore, the model predicts that in going from evaporation to combustion, the system will pass through a characteristic value of reaction rate at which heat is no longer required from the environment, but rather is supplied to it. This corresponds to a transition from a kinetics-controlled regime to a diffusion-limited regime. It seems likely that ignition is associated with such a transition. Based on this criterion, the theory predicts that ignition requires the following relationship between droplet diameter D and oxidizer ambient temperature T:

$$\log D^2 = \frac{E}{2.3R}\left(\frac{X_o}{i} + 1\right) - \frac{1}{T} + \log \frac{Kb_c}{4B} \qquad (3)$$

where

E = activation energy,

R = universal gas constant,

X_o = ambient oxygen weight fraction,

i = stoichiometric ratio (moles O_2/moles fuel),

$\varkappa$ = diffusivity of fuel vapor,

B = reaction rate constant, and

b_c = critical reaction parameter for ignition.

The quantity b_c includes the weight fractions of fuel X_F and oxygen X_o, the surface temperature of the droplet T_s, and the thermodynamic properties of the system such as heat of combustion Q, heat of vaporization L, and the specific heat of the vapor Cp. It is apparent that numerical solutions of such an equation involving a multiplicity of independent parameters would be of doubtful value as a comparison with appropriate experimental measurements. However, a comparison of the functional relationships of the experimental data with that predicted by theory is significant. A logarithmic dependency of the square of the characteristic droplet diameter on the reciprocal of the ignition temperature, predicted by Eq. (3), is demonstrated by the experimental data in Fig. 12. The dashed line is

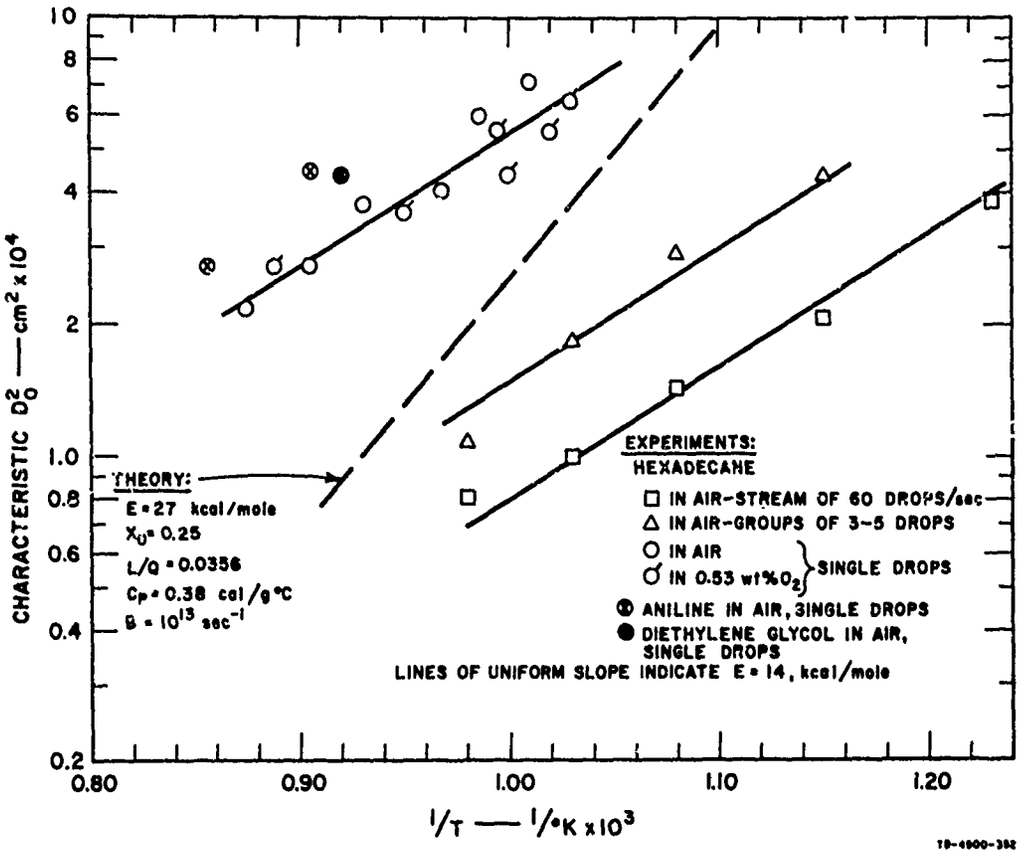


FIG. 12 COMPARISON OF THEORETICAL AND EXPERIMENTAL DROPLET IGNITION RESULTS

a theoretical computation based on selected values for the system parameters.[16] Obviously, a better fit between theory and experiment could have been forced by adjustment of these values.

The slope of the lines suggest that hexadecane droplets exhibit an effective activation energy for ignition of 14 kcal/mole, independent of their state of aggregation. However, the intercepts of these parallel lines depend markedly on the droplet-droplet proximity, suggesting that degree of closeness of the droplets affects some parameter in the last term of Eq. (3). One would not expect the thermodynamic properties of the system contained in this term to be affected by droplet-droplet interaction. But the quantity b_c is inversely related to X_F, the weight fraction of fuel vapor. Hence, the progressively lower values of intercept displayed in Fig. 12 by the lines drawn through the data points for

groups and streams of droplets respectively, suggests that the observed lower ignition temperatures for a given size droplet are a result of an enhanced fuel vapor concentration in (or a lower oxygen concentration) in the vicinity of the droplet.

There are not sufficient data on the other fuels, aniline and diethylene glycol, to evaluate activation energies. It would be expected that each fuel would exhibit its own activation energy characteristic of the chemical mechanism by which it reacts with oxygen. At present, there is no way to predict the value of this parameter.

The experimental data suggest that an enhancement in the weight fraction of oxygen in the oxidizer has no effect on the ignition temperature, within the limits of experimental error. The theory predicts[17] that a change in oxygen weight fraction from 0.25 to 0.50 would raise the ignition temperature of a droplet of specified size by only 5 percent, a variation too small to resolve by this experimental technique.

The data (Fig. 12) indicate that a given diameter droplet of aniline requires a higher ignition temperature than a like-sized droplet of hexadecane. Based on an examination of the thermodynamic properties of these fuels (Table III) it seems possible that this may be attributable to their substantially different stoichiometric ratios, i. The theory is in qualitative agreement here, also, for it predicts a decrease in ignition temperature when the value i is raised, other parameters being held constant.

Table III

THERMODYNAMIC PROPERTIES OF FUELS

Fuel	Boiling Point, °C	L/Q	i
Aniline	183	0.021	7.8
Diethylene Glycol	245	0.051	5.0
Hexadecane	288	0.021	24.5

3. Wake Ignition and Burning

Neither the still photographs nor the schlieren movies show an unequivocal locus of the flame front associated with a free-falling burning droplet. The photographs of pendent drops (Fig. 10), however, demonstrate the profound effect of relative droplet velocity on the flame shape. The appearance of a luminous zone in the wake of a falling droplet suggests that ignition occurs in this region. The movies indicate that in many cases the luminous region follows the droplet in its trajectory, but never overtakes and envelops it. It seems likely, therefore, that in some instances the "burning" droplets observed in our experiments may have been in fact vaporizing droplets with luminous flames consuming the vapors in their wakes. As mentioned earlier, this notion is consistent with the measured evaporation constants under certain conditions. It is evident from the observed variation in characteristic diameter for ignition with droplet spacing (stream frequency, Fig. 7) that such wake flames are reliable ignition sources for droplets that encounter them.

III CONCLUSION

In spite of the complexity of the ignition process, the results of our experiments could be correlated qualitatively with theoretical models that seem to represent a reasonable approximation to the physical situation of a fuel droplet suddenly exposed to a hot, oxidizing atmosphere. Our data indicate that a measurable quantity of practical interest is the ignition lag τ. This parameter depends strongly on the temperature of the atmosphere and on the droplet-droplet spacing, in addition to the chemical nature of the fuel, but appears to be only weakly affected by the oxygen concentration in the oxidizer. The ignition lag seems to be independent of the initial droplet size for droplets large enough to ignite at all. This trait insures that droplets with initial diameters D_o smaller than a characteristic value D_{cr}, given by $D_{cr} = \sqrt{\epsilon\tau}$, will not ignite during their lifetimes.

Caution must be used in applying the results of our study of single droplet ignition to the ignitability of an aerosol cloud. For instance, if an aerosol cloud is exposed to a strong ignition source such as a flame associated with the explosion that produces the cloud, then the quantity of interest is the aerosol concentration relative to the lower lean flammability limit. Auto-ignition of droplets can be ignored. In the absence of a strong source, auto-ignition is possible if the cloud is flammable and is exposed to a hot atmosphere, as from shock heating for example. The character of the ignition will depend on whether or not the cloud contains droplets with diameters greater than the characteristic diameter corresponding to the given conditions. If the cloud contains such droplets, then single droplet ignition of the type observed in our study is probable if the time of exposure of the aerosol cloud to a hot atmosphere is comparable to or longer than the ignition lag. The resulting single droplet flame can then spread throughout the cloud. Ignition and burning of single large droplets, but without propagation, is still possible when the over-all concentration of aerosol is below the lower

lean flammability limit. Single drop ignition is favored by a high gas temperature, i.e., in the region where characteristic diameter is small. If the aerosol cloud does not contain droplets with diameters greater than the characteristic diameter, auto-ignition may occur only as a result of the formation of a flammable vapor-air mixture due to evaporation of much of the aerosol cloud. Such a condition is favored by a moderate gas temperature, i.e., in the region where characteristic diameter is large.

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13. ABSTRACT

By means of photographic techniques, the size histories, ignition lags, and loci of ignition of small (100-300 microns diameter), single, freely fall[illegible] droplets suddenly exposed to a hot, oxidizing atmosphere in a furnace were determined [illegible] function of initial droplet size, oxidizer temperature, fuel composition, and droplet spacing. The results show that ignition lag depends significantly on the temperature of the atmosphere, on the droplet-droplet spacing, and on the chemical nature of the fuel, but it appears to be only weakly affected by the oxygen concentration in the oxidizer. The ignition lag seems to be independent of the initial droplet size if the droplets are large enough to ignite at all. This characteristic insures that droplets with initial diameters smaller than a characteristic value will not ignite during their life-times. In spite of the complexity of the ignition process, the experimental results correlate satisfactorily with theoretical models that seem to represent a reasonable approximation to the physical situation of a spontaneously igniting fuel droplet.

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Explosive dissemination						
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Autoignition						
Oxidizer						
Fuel composition						
Combustible aerosol						
Fuel droplets						
Wake ignition						
Flashing						

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