VAPORIZATION OF DROP SYSTEMS IN VARIOUS MEDIA

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We have studied the vaporization of 2 mm drops of benzene, C_6H_6, methanol, CH_3OH, and triethylamine, $(C_2H_5)_3N$, in air and in the saturated vapors of a 98% solution of nitric acid, HNO_3.

Experiments were carried out in a glass chamber containing a two-degrees-of-freedom sample manipulator equipped with glass drop supports. The distance between drops was varied from 10^{-4} m to $5 \cdot 10^{-3}$m. The rate of vaporization was determined either by direct microscopic measurement of the drop diameter, or by photographing. The experiments in HNO_3 vapors were carried out with free evaporation of the acid from several Petri dishes placed in the bottom of the chamber. Vapor saturation was assumed when drops of the acid no longer evaporated.

Experiment showed that drop vaporization kinetics followed the Sreznevskii law, $dS/dt = K = \mathrm{const}$, in both neutral and chemically active media. For each liquid, the rate constant for individual drop vaporization in saturated HNO_3 vapors K_X was greater than the rate constant for vaporization in air K_H (Table 1). The high rate of individual drop vaporization in the chemically active medium can be understood if the assumption is made that a reaction zone is set up around the drop, thereby diminishing the depth of the vapor layer around the drop and increasing the vapor concentration gradient at the drop surface.

Experiments on the vaporization of two-drop systems (C_6H_6—HNO_3, CH_3OH—HNO_3, $(C_2H_5)_3N$—HNO_3) in air showed the rates of evaporation from benzene, methanol, and triethylamine drops to increase as the drop separation was diminished, the tendency being to approach the rate of evaporation of the individual drop in saturated nitric acid vapors (Fig. 1). The vaporization kinetics followed the Sreznevskii law when the distance of separation was greater than the drop radius. Departures from this law were observed when the distance of separation was less than the drop radius, the time variation of the drop radius being then covered by a power law, the exponent falling off from 2 to 1 as the distance of separation was reduced to eventual contact.

The burning of drop systems in air has been discussed in [1-3]; there it was shown that the combustion rate is a non-monotonic function of the distance of drop separation, being a maximum when the drop flames touch and a minimum when the drops themselves are in contact.

The kinetics of two-drop system vaporization in air and in saturated nitric acid vapors follow the Sreznevskii law. Drop interaction in such systems can therefore be characterized by expressing the vaporization rate constant as a function of drop separation, i.e., by writing K(r). Figure 2 shows the K(r) function for the various liquids studied here. It is seen that the vaporization rate constant for methanol

TABLE 1. Vaporization Rate Constants, $K \cdot 10^8$, m^2/sec, and Their Ratios

Compound	K_{H}	K_{X}	$K_{\mathrm{X}}/K_{\mathrm{H}}$
Benzene	5,74	6,12	1,10
Methanol	3,78	5,08	1,33
Triethylamine	4,72	6,58	1,40

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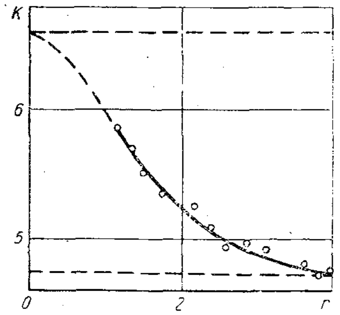

Fig. 1

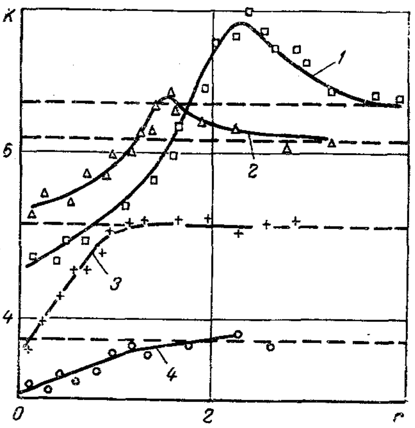

Fig. 2

Fig. 1. Relation between the vaporization rate constant, $K \cdot 10^8$, m^2/sec, for triethylamine drops and the distance of separation, $r \cdot 10^3$, m, from a drop of 98% nitric acid, for vaporization in air.

Fig. 2. Relation between the vaporization rate constant, $K \cdot 10^8$, m^2/sec, and the distance of drop separation, $r \cdot 10^3$, m, for vaporization in saturated nitric acid vapors: 1) triethylamine; 2) benzene, 3) methanol, 4) vaporization of a two-drop methanol system in air.

passed through a minimum at $r = 10^{-4}$ m, and then steadily increased with increasing distance of separation, approaching K_X as a limit. The vaporization rate constants for benzene and triethylamine drops were not monotonic functions of the distance of drop separation, being a minimum at $r = 10^{-4}$, rising with increasing separation to a value in excess of K_X at $r \sim 2 \cdot 10^{-3}$ m, and then falling gradually to K_X.

The observed alteration in the rate of drop evaporation with increasing distance of drop separation can be explained in terms of the interaction of two factors: reaction zone overlap, which tends to diminish the vaporization rate, and natural convection around the drop system which tends to increase it. The effect of natural convection can be neglected in the case of methanol where the molecular weight of the vapors is close to the molecular weight of air (32 and 29, respectively). Schlieren photographs showed the vapor layer around the methanol drop to be more nearly spherical than the vapor layers around drops of the other liquids. Change in the distance of separation of methanol drops should therefore do no more than alter the degree of reaction zone overlap, thus leading to a monotonic variation in the vaporization rate.

The fact that K(r) proves to be a non-monotonic function of r under natural convection can be understood by considering the effect of increasing drop separation on the type of streamline flow established around the drop system. At close approach, natural convective streaming occurs around the drop pair as a single system. The diameter of the entire system, a quantity which increases with increasing distance of drop separation, is therefore the diameter to be substituted into the expression for the Archimedian number, Ar, which characterizes natural convective flow [4]. K should then increase with increasing r. Streaming occurs around each drop separately at greater distances of separation, and the diameter to be substituted in the expression for Ar will then be that of the individual drop. There should, therefore be a certain distance of separation at which Ar and the vaporization rate constant K assume maximum values, just as observed experimentally.

NOTATION

r	is the distance between drop edges;
S	is the drop surface;
t	is the time;
K	is the reaction rate constant;
Ar	is Archimedes number.

Subscripts

H refers to neutral medium;

X refers to chemically active medium.

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