Evaporation Rates and Vapor Pressure of Some Fluoro- and Trifluoromethyl-Substituted 2-Hydroxy-4-methoxybenzophenones

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The evaporation rates and vapor pressures for six new fluorine and trifluoromethyl substituted 2-hydroxy-benzophephenones are reported. The evaporation rates for 3'-fluoro-, 2'-trifluoromethyl-, and 4'-trifluoromethyl-2-hydroxy-4-methoxybenzophenone are lower than that of the parent compound.

THE o-hydroxybenzophenones are useful as protective ultraviolet absorbers for plastics. The evaporation rates and vapor pressure are reported for two commerical ultraviolet absorbers, 2-hydroxy-4-methoxy-benzophenone and 2,4-dihydroxybenzophenone, and six new substituted 2-hydroxybenzophenones which were synthesized for evaluation as protective absorbers for organic coatings for space vehicles as reported by Horman (3) and by Gray (2). These data were obtained by a modification of the method of Verhoek and Marshall (5) and Schmitt and Hirt (4).

EXPERIMENTAL

Evaporation rates were measured by determining the amount of solid material escaping from a free surface as a function of temperature and time. The stage and collector are shown in Figure 1. The sample stage is a rhodium-plated copper cylinder (A) bored to hold a 150-watt cartridge-type heater (B). A thermocouple is housed in an adjacent hole (C) which extends to within a millimeter of the sample-holding depression in the stage

(D). Both the heater and the thermocouple are connected to a Minneapolis Honeywell Pulse Pyro-vane controller. The pressure is monitored either by a thermocouple gage or an ionization gage depending on the pressure range. Both the thermocouple and the ionization gage were connected to a Consolidated Type GIC-110A instrument. In operation, the diffusion pump side of the apparatus was pumped to a low pressure (10^{-5} to 10^{-6} mm. of Hg) while the stage side was rough pumped to 10 mm., keeping the stage at room temperature. At the start of the run, the stage side was opened to the low pressure diffusion pump side (E), the heater was turned on, and liquid nitrogen was added to the collector assembly (F). A pressure of 10^{-6} mm. could be reached in approximately 1 to 2 minutes, and the stage would heat from ambient temperature to the desired temperature in less than one minute. Therefore, in a usual run of one to two hours, the rise time does not present a significant source of error. The evaporated material was collected on the liquid-nitrogen cooled concave collector (F), washed off with 95% ethanol, made up to volume, and the concentration determined by quantitive ultraviolet spectrophotometry. The stage temperature as recorded on the pyrometer was checked periodically

Table I. Evaporation Rate Data

Compound	Temperature, ° K.	Evaporation Rate, Grams/Cm.³/Sec.	Vapor Pressure, Mm.
2-Hydroxy-4-methoxybenzophenone	308	1.57×10^{-7}	3.12×10^{-6}
	313	2.40×10^{-7}	4.81×10^{-6}
	323	3.26×10^{-7}	6.65×10^{-6}
2,4-Dihydroxybenzophenone	323	1.08×10^{-7}	2.28×10^{-6}
	333	1.86×10^{-7}	3.98×10^{-6}
	353	1.54×10^{-6}	3.38×10^{-5}
	363	4.27×10^{-6}	9.51×10^{-5}
2'-Fluoro-2-hydroxy-4-methoxybenzophenone	308	1.05×10^{-6}	2.02×10^{-5}
	313	1.99×10^{-6}	3.86×10^{-5}
	318	3.96×10^{-6}	7.74×10^{-5}
3'-Fluoro-2-hydroxy-4-methoxybenzophenone	323	1.05×10^{-7}	2.05×10^{-6}
	333	1.11×10^{-7}	2.21×10^{-6}
	343	1.48×10^{-7}	2.99×10^{-6}
4'-Fluoro-2-hydroxy-4-methoxybenzophenone	323	9.04×10^{-8}	1.77×10^{-6}
	333	9.32×10^{-8}	1.85×10^{-6}
	343	2.00×10^{-7}	4.04×10^{-6}
2'-Trifluoromethyl-2-hydroxy-4-methoxybenzophenone	323	5.50×10^{-8}	9.81×10^{-7}
	333	6.32×10^{-8}	1.15×10^{-6}
	343	7.03×10^{-8}	1.30×10^{-6}
	363	7.86×10^{-8}	1.50×10^{-6}
3'-Trifluoromethyl-2-hydroxy-4-methoxybenzophenone	313	1.37×10^{-6}	2.41×10^{-5}
	318	3.09×10^{-6}	5.45×10^{-5}
	323	4.63×10^{-6}	8.26×10^{-5}
4'-Trifluoromethyl-2-hydroxy-4-methoxybenzophenone	313	1.34×10^{-6}	2.34×10^{-5}
	323	3.59×10^{-6}	6.40×10^{-5}
	333	1.05×10^{-5}	1.91×10^{-4}
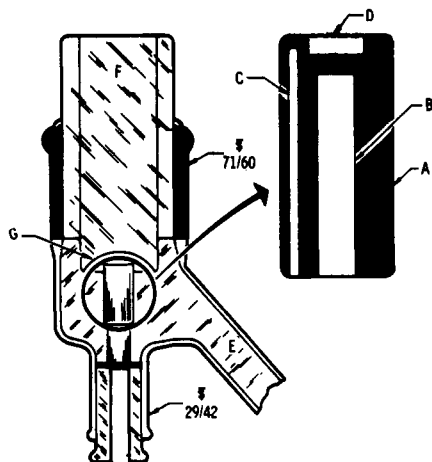
Figure 1. Heating stage and collector assembly—
evaporation rate apparatus

Figure 2. Evaporation rates

by using the stage as a melting point block for zone-refined samples in the range 50° to 150° C. The precision of the stage temperature was judged to be ± 0.5° C.

DISCUSSION

As the area of the sample depression, the temperature, and the amount of material transferred per second were known, the vapor pressure was determined by using the equation

$$P_{mm} = 17.14G(T/M)^{1/2}$$

where P_{mm} is the vapor pressure in millimeters of mercury, G is the evaporation rate in grams per square centimeter per second, M is the formula weight, and T is the absolute temperature (1). The data are given in Table I and Figure 2. The volatilities of 2-hydroxy-4-methoxy-3'-fluorobenzophenon , 2-hydroxy-4-methoxy-4'-fluorobenzophenone, and 2-hydroxy-4-methoxy-2'-trifluoromethylbenzophenone are lower than 2,4-dihydroxybenzophenone and 2-hydroxy-4-methoxybenzophenone at temperatures above 60° C. Figure 2 indicates that the vaporization rate of 2,4-dihydroxybenzophenone will exceed that of 2-hydroxy-4-methoxybenzophenone at temperatures higher than 342° K. (69° C.). Such an extrapolation is not valid,
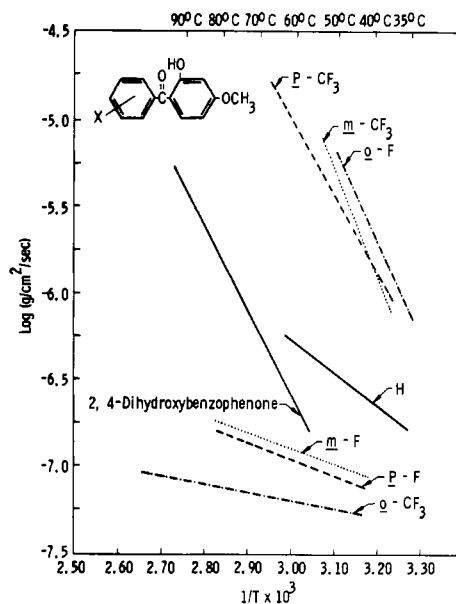
however, since these data are for evaporation rates of solid samples and 2-hydroxy-4-methoxybenzophenone will be liquid at temperatures above 65° C. An evaporation curve for the liquid will have an entirely different slope.

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Dielectric Properties of Phosphoric Acid Solutions at 25° C.

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MATHEMATICAL DESCRIPTIONS of the absorption-dispersion phenomena of electrolytic solutions have been derived from measurements of their dielectric properties (3-7). The present measurements were made to determine the static dielectric constants of phosphoric acid solutions; previously developed mathematical expressions were used in the treatment of the data. Similar measurements were made on sodium chloride solutions to establish the validity of the results by comparison with published values of the static dielectric constants.

EXPERIMENTAL

Phosphoric acid solutions were prepared by dilution of concentrated stock acid that had been purified by crystallization as $2H_3PO_4 \cdot H_2O$; concentrations were established by density (2). Sodium chloride solutions were prepared by weight from conductance water and dried reagent-grade salt. The conductance of the water did not exceed 2×10^{-6} ohm^{-1}cm.$^{-1}$, and all calculations were based on the 1961 atomic weights (11). The low-frequency conductance of phosphoric acid (13, 16) and sodium chloride solutions (1) has been reported.