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Note

KINETICS OF EVAPORATION OF SOME LIQUIDS BY THERMOGRAVIMETRY

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Latent heat of evaporation is one of the decisive factors in the design and operation of chemical plants [1]. Brennan et al. [2] have shown that the heat of evaporation of a liquid and the activation energy of evaporation, $E_{\text{act}}^{\text{evap}}$, are found, as expected, to be numerically similar. We present here some results on the kinetics of evaporation of five liquids (selected at random) based on TG data.

EXPERIMENTAL

All the liquids were purified by standard techniques [3]. The purity was checked by infrared and ^{1}H NMR spectra. The infrared spectra were taken on a Perkin-Elmer 377 spectrophotometer in the range 600–2000 cm^{-1} as a thin film sandwiched between NaCl optics while the ^{1}H NMR spectra were recorded on a Varian EM 390, 90 MHz spectrophotometer in $CDCl_3$ or DMSO-d_6 using TMS as external standard. The TG and DTA data were recorded and handled as decribed in ref. 4.

RESULTS AND DISCUSSION

The mechanism of evaporation of a liquid in the vicinity of its boiling point can be studied by employing the thermogravimetric technique. Kumar et al. [4] have evaluated the kinetics of degradation of some transition metal salts by thermogravimetry using Zsako's method [5]. However, this method is

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TABLE 1

TG and DTA data on the evaporation of some liquids (E_{act}^{evap} and all ΔH_{evap} values in kcal mol^{-1})

Liquid	E_{act}^{evap}	ΔH (TG)	ΔH (DTA)	ΔH (lit. [8])	B_0
Triethylphosphate	13.6	12.4	11.3	11.5	0.022433
1,4-Dioxane	9.9	8.5	8.4	8.5	0.0073962
Ethylacetate	9.9	8.4	8.3	8.3	0.0180737
Acetonitrile	9.4	8.2	8.1	8.2	0.0023710
n-Octadecane	17.8	17.4	–	15.4	0.013182

designed to study the kinetics of unitary processes. The process of evaporation, i.e.

$$\text{liquid} \xrightarrow{\Delta} \text{gas}$$

is, by all means, a reversible process and represents a physical change brought about by overcoming "residual" chemical forces. It will be of some interest to study the kinetics of evaporation of a liquid under the conditions of thermogravimetry. None of the selected liquids has a labile proton and, therefore, they are free from extensive hydrogen bonding. Table 1 gives the values for E_{act}^{evap} and ΔH_{evap}. The latter has been evaluated using DTA [6] and TG [7] techniques. In all the liquids, except *n*-octadecane, an endotherm is noticed corresponding to evaporation upon heating. However, in the case of *n*-octadecane, an exotherm was noticed, presumably due to its combustion, which concurs with its evaporation. It is also worth noting that the values of ΔH_{evap} obtained by Stepin et al.'s method [7] (TG) are in slight error. This is not altogether unexpected since the calculation of ΔH_{evap} based on Stepin et al.'s method (loc. cit.) assumes unit activities of the components in the condensed phase and also that the fugacities of gaseous components are the same as their pressures at all temperatures. The values of ΔH_{evap} obtained by DTA have been used as reference and a correction factor, δ, defined as

$$\delta = \Delta H_{evap}(\text{TG}) - \Delta H_{evap}(\text{DTA})$$

for a reference liquid may be applied. In our case we used 1,4-dioxane as the reference liquid ($\delta = +2.1$ kcal mol^{-1}). The literature values for ΔH_{evap} have also been included in Table 1 [8].

The most important point is, however, the "order" of the reaction involving the process of evaporation. All the liquids have a zero order evaporation process. This, in the present case, is unavoidably attributed to the fact that the concentration of a pure liquid is constant, the density changes with temperature notwithstanding. The values of E_{act}^{evap} are more or less quite close to ΔH_{evap}.

From these studies it is concluded that:

(i) thermogravimetry may be used as a tool for understanding phase-change mechanisms, provided these are accompanied by weight changes;

(ii) the process of evaporation of a liquid exhibits Arrhenius-type behaviour; and

(iii) Zsako's method, which was devised to study the kinetics of unitary processes, may also be applied to systems which have a homogeneous condensed phase and are in dynamic equilibrium.

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