

sponding relationship for the two trans acids depends upon whether the comparison is made with the metastable or stable form of elaidic acid.

The standard deviations of the experimental data from the curves in Figure 1 and from the linear $\log N$ vs. $1000/T$ plots for each acid fall between 0.05° and 0.12° C. and between 0.04° and 0.12° C., respectively.

The isolation and characterization of the stable modification of elaidic acid will be reported in a forthcoming publication (4).

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The authors are indebted to George I. Pittman for drawing the figure.

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Densities of Molten BiCl_3 and AlCl_3 Mixtures

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The "float" method was used to measure the liquid densities of AlCl_3 - BiCl_3 mixtures containing 0.0, 20.0, 35.0, and 60.0 mole % of AlCl_3 . All mixtures were studied over a range of temperatures and the data fitted to equations of the form $\rho = \alpha - \beta t$ by a least-squares analysis. Molar volumes showed negative deviations from additivity as large as 13%.

MOLTEN salt mixtures that are acidic in the Lewis sense are good solvents for stabilizing lower oxidation states (3). For example, AlCl_3 - NaCl mixtures have been used as solvents for spectrophotometric studies of the lower oxidation states of bismuth (1). Density measurements on these mixtures were necessary for the calculation of optical extinction coefficients but were also of interest in themselves because of the very large deviations from linearity which were observed (2). The purpose of the present work was to determine densities on another acidic solvent system of spectroscopic interest—namely, AlCl_3 - BiCl_3 mixtures. Again, the densities themselves should be of interest especially when compared with the results for AlCl_3 - NaCl mixtures.

EXPERIMENTAL

Density Determination. The float method was used for measuring density. This consisted of measuring the temperature at which quartz floats of known density neither fell nor rose in the liquid under study. The apparatus has been described previously (2). Minor modifications were required to measure densities greater than that of quartz. The first was to seal a length of platinum wire into the

quartz floats to produce a float density greater than that of quartz alone. The second modification was the use of a very low density float on top of the density floats to hold the latter just under the surface. This prevented the density floats from sticking at the surface because of surface tension. This top float was simply a flat-bottomed bubble of quartz, made a little heavier on the flat side so that this side would stay down, and of sufficient diameter to prevent the density floats from passing or becoming wedged next to it in the container tube. The top float density (1.8 grams per cc.) was considerably less than that of the liquids under study. Thus, it remained on the surface during all measurements.

Materials. The AlCl_3 was prepared from high purity aluminum metal and HCl by the method described by Bjerrum, Boston, and Smith (1). The BiCl_3 was prepared by the reaction of zone refined, 99.9999% bismuth metal with chlorine gas followed by several successive distillations.

RESULTS AND DISCUSSION

The density results are summarized in Table I. At each composition the temperature dependence of the density ρ is given by the usual expression, $\rho = \alpha - \beta t$, where

Table I. Density Equations for AlCl_3 - BiCl_3 Mixtures

Composition, Mole % AlCl_3	$\rho = \alpha - \beta t$		Std. Dev. $\times 10^3$, Grams/Cc.	Molar Volume at 220° C., Cc./Mole	Exptl. Temp. Range, $^\circ$ C.	Reference
	α , grams/cc.	$\beta \times 10^3$, grams/ cc./ $^\circ$ C.				
0.0	4.433	2.26	0.8	80.12	411-479	
0.0	4.417	2.20	1.0	80.19	239-331	(5)
20.0	3.837	1.90	0.8	81.59	201-84	
35.0	3.427	1.71	3.8	82.42	188-400	
60.0	2.751	1.43	2.6	84.61	167-281	
100.0	1.734	2.33	1.7	109.2	202-21	(2)

α and β are constants and t is the temperature in °C. Each composition was measured at four temperatures, except the 35.0 mole % AlCl_3 which was measured at six temperatures. The standard deviations for the least squares fit and the experimental temperature ranges are listed in Table I. Molar volumes were calculated at 220°C. for direct comparison with previous volume measurements on the AlCl_3 -NaCl system (Table I).

A pycnometric method was used by Keneshea and Cubicciotti (5) to measure the density of pure BiCl_3 . Their results are listed in Table I and agree quite well with the results reported here. More recently, Johnson and Cubicciotti (4) used the float method to obtain BiCl_3 liquid densities at higher temperatures ranging up to the critical temperature. These authors compared their high temperature results with the low temperature pycnometric results (5) and found them to be in good agreement.

Molar volumes for the AlCl_3 -NaCl system showed a maximum negative deviation from linearity of the order of 20%. This was attributed at least in part to the strong acidic nature of AlCl_3 resulting in the formation of AlCl_4^- and Al_2Cl_7^- . The AlCl_3 - BiCl_3 system showed a maximum negative deviation of the order of 13% at comparable com-

positions and temperatures. Although this may seem surprising considering the acidic nature of BiCl_3 , it probably is just another indication of the extreme acidity of AlCl_3 relative to most other solvents.

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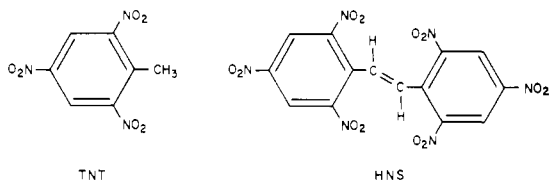
Heats of Combustion of *trans*-Stilbene and *trans*-2,2',4,4',6,6'-Hexanitrostilbene (HNS)

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The standard heats of combustion, $\Delta H_c^\circ_{298}$, of *trans*-stilbene (c) and *trans*-2,2',4,4',6,6'-hexanitrostilbene(c) were measured in an oxygen bomb calorimeter and were -1759.28 and -1535.54 kcal. mole⁻¹, respectively. Estimated uncertainties of these results, respectively, were 0.93 and 1.08 kcal. moles⁻¹ including contribution of errors from both random and systematic sources. With these results, the standard heats of formation, $\Delta H_f^\circ_{298}$, of *trans*-stilbene(c) and *trans*-2,2',4,4',6,6'-hexanitrostilbene(c) were -32.68 and -13.89 kcal. mole⁻¹, respectively. The standard heats of formation of the gas phases were -12.0 and +29.2 kcal. mole⁻¹, respectively. In the light of these results, and analogous data for toluene(g) and trinitrotoluene(g), the addition of six nitro groups to *trans*-stilbene may be interpreted as weakening the central C=C bond by 34.1 kcal. mole⁻¹.

RECENTLY, Shipp successfully synthesized *trans*-2,2',4,4',6,6'-hexanitrostilbene, henceforth designated as HNS (13, 14). The close relationship of HNS to 2,4,6-trinitrotoluene (TNT) immediately becomes obvious by a comparison of their structural formulas:



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HNS is a solid explosive somewhat less sensitive than TNT. Because of its low vapor pressure and good heat stability, it is suitable for applications requiring storage in a high vacuum and subjection to temperature extremes, such as may be encountered in the exploration of the moon's surface. To obtain information about the energy of HNS, as is required to use it effectively as an explosive, the authors have determined the heat of formation with respect to the elements. This objective of the present work was accomplished by measuring the heat of combustion of HNS.

It also was convenient to consider as a subsidiary objective the effect of adding six nitro groups to the aromatic nuclei of *trans*-stilbene on the C=C bond linking them. This effect may be estimated by combining combustion