

A CALORIMETRIC AND PMR STUDY OF THE CHLORINATION OF SOME *t*-BUTYL COMPOUNDS BY ANTIMONY PENTACHLORIDE

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Abstract—*t*-BuCl and *t*-BuOH are instantaneously chlorinated by SbCl₅ in dilute solution to give 1,2-dichloro-2-methylpropane, SbCl₃ and HCl or H₂O, respectively. The enthalpy changes, in kJ·mol⁻¹, for the chlorination reaction with reactants and reaction products in 1,2-dichloroethane solution are: *t*-BuCl - 72.0 ± 0.2 and *t*-BuOH - 93.6 ± 1.2. Rapid chlorination of *t*-BuOAc does not take place unless SbCl₅ is present in excess, the enthalpy change for the reaction being -100 ± 2 kJ·mol⁻¹. The initial step of the chlorination reaction is considered to be interaction between SbCl₅ and a lone electron pair at the atom bound to the *t*-Bu group.

IN A calorimetric study of the formation of donor-acceptor adducts between antimony pentachloride and alkyl carboxylates it was found that enthalpy change for the interaction of *t*-BuOAc was twice as large as that of comparable esters.¹ It was concluded that *t*-BuOAc reacted in a different way and possibly underwent a chlorination reaction. It is known that *e.g.* *t*-BuCl is easily chlorinated by SbCl₅ to 1,2-dichloro-2-methylpropane.^{2, 3} In order to obtain information about the action of SbCl₅ on *t*-Bu compounds we undertook a calorimetric and PMR study of the systems *t*-BuX-SbCl₅ (X = Cl, OH, OCOCH₃) in an inert solvent.

RESULTS

PMR spectra of CHCl₃ solutions of SbCl₅ and an equivalent amount of *t*-BuCl and *t*-BuOH, respectively, showed the same pair of resonance signals identical with those of 1,2-dichloro-2-methylpropane in CHCl₃ solution. The initial concentration of the reactants was 0.5 mol·l⁻¹ and the solutions were found to be stable.

Spectra of freshly prepared samples of the *t*-Bu compounds of initial concentration of 0.1 mol·l⁻¹ with SbCl₅ in excess showed signals of 1,2-dichloro-2-methylpropane and in the *t*-BuOAc sample an additional one which was identified as the resonance signal of the Me group in the SbCl₅-HOAc donor-acceptor adduct. On standing a new pair of signals appeared close to the diminishing signals of 1,2-dichloro-2-methylpropane. These signals were identical with those found in the spectrum of a sample of pure SbCl₅ to which *t*-BuCl had been added under cooling. In the spectrum of a sample to which a known amount of CHCl₃ had been added as an internal standard the two signals from the reaction product appeared at 1.7 and 3.8 ppm, respectively and the chloroform signal at 7.2 ppm. The relative intensities of the signals showed that the reaction product most probably was 1,2,3-trichloro-2-methylpropane.

TABLE 1. ENTHALPY OF REACTION OF *t*-BuX(1) WITH SbCl₅ IN EXCESS IN 1,2-DICHLOROETHANE SOLUTION. THE INITIAL CONCENTRATION OF *t*-BuX 0.005–0.014 AND OF SbCl₅ 0.02–0.03 mol.l⁻¹.

<i>t</i> -BuX	$-\Delta H_1/\text{kJ} \cdot (\text{mol } t\text{-BuX})^{-1}$
<i>t</i> -BuCl	70.8 ± 2.0
<i>t</i> -BuOH	156.0 ± 0.8
<i>t</i> -BuOCOCH ₃	146.6 ± 0.8

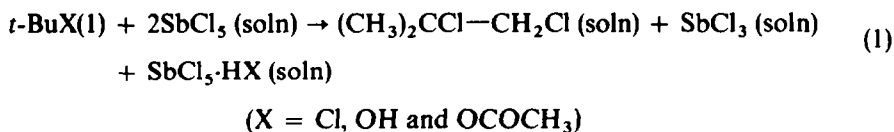
TABLE 2. ENTHALPY OF REACTION OF SbCl₅(1) WITH *t*-BuX IN EXCESS IN 1,2-DICHLOROETHANE SOLUTION. THE INITIAL CONCENTRATION OF *t*-BuX 0.014 AND OF SbCl₅ 0.010 mol.l⁻¹

<i>t</i> -BuX	$-\Delta H_2/\text{kJ} \cdot (\text{mol SbCl}_5)^{-1}$
<i>t</i> -BuCl	73.8 ± 0.2
<i>t</i> -BuOH	97.6 ± 0.8
<i>t</i> -BuOCOCH ₃	50 – 57

TABLE 3. ENTHALPY OF SOLUTION OF VARIOUS SUBSTANCES IN 1,2-DICHLOROETHANE.

Substance	Conc./mol.l ⁻¹	$\Delta H_3/\text{kJ} \cdot \text{mol}^{-1}$
<i>t</i> -BuCl (1)	0.07	1.59 ± 0.03
<i>t</i> -BuOH (1)	0.03–0.05	15.35 ± 0.03
SbCl ₅ (c)	0.004–0.010	9.12 ± 0.03

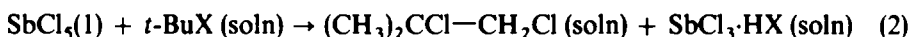
Results of the calorimetric experiments with SbCl₅ in excess in the calorimetric liquid are summarized in Table 1. The ΔH_1 values refer to reaction (1):



The given results are mean values of three to four experiments. In all experiments the reaction took place instantaneously and the main reaction was completed within two min. The temperature change during the after periods showed, however, that a slow exothermal secondary reaction occurred which became more pronounced with increasing excess of SbCl₅. The secondary reaction influenced only to a small extent the determination of the enthalpy values as the initial and final resistance values were obtained graphically (*cf.* Ref. 4). The ΔH_1 value given for *t*-BuOAc is derived from the two experiments reported in Ref. 1 plus one in addition.*

* The $-\Delta H$ value given in Ref. 1 is 4 kJ · mol⁻¹ too large on account of using too long a main period in the evaluation of the experiments.

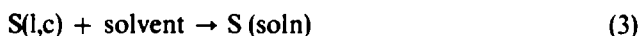
The results of the calorimetric experiments with the *t*-Bu compounds in excess in the calorimetric liquid are summarized in Table 2. The ΔH_2 values for *t*-butyl chloride and *t*-butanol refer to reaction (2):



These reactions were instantaneous and no secondary reactions could be detected in the *t*-BuCl experiments and occurred only to a small extent in the experiments with *t*-BuOH. The ΔH_2 values are mean values of duplicate runs.

The time-temperature curve in the experiments with *t*-BuOAc in excess was complex and indicated a rapid exothermic process, an intervening endothermic one and a slow exothermic reaction. The value in Table 2 gives the size of the enthalpy change of the first rapid process.

Enthalpies of solution of various substances are given in Table 3.



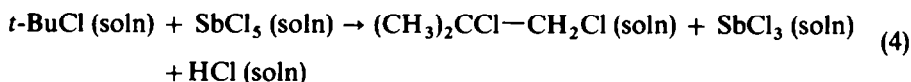
The enthalpy values are mean values of three to four experiments. No difference could be detected between ΔH values found when dissolving SbCl_3 in 1,2-dichloroethane containing about $5 \cdot 10^{-4}$ mol \cdot l $^{-1}$ of H_2O either directly or after addition of SbCl_3 (0.02 mol \cdot l $^{-1}$) prior to the experiment. However, if larger amounts of H_2O were present the interaction with SbCl_3 was noticeable. Dissolution of SbCl_3 (0.010 mol \cdot l $^{-1}$) in solvent containing 0.05 mol \cdot l $^{-1}$ of H_2O gave an apparent enthalpy of solution of 6.2 ± 0.2 kJ \cdot mol $^{-1}$. Accordingly, the apparent enthalpy of interaction between SbCl_3 and water at this concentration is -2.9 kJ \cdot mol $^{-1}$.

To the random errors expressed as single standard deviation of the mean have been added estimates of errors due to secondary reactions in Tables 1 and 2.

Experiments in which *t*-BuCl (0.01 mol \cdot l $^{-1}$) was dissolved in 1,2-dichloroethane containing 0.02 mol \cdot l $^{-1}$ of TiCl_4 showed that TiCl_4 and *t*-BuCl do not give any measurable enthalpy of interaction under these conditions.

Summary of calorimetric results

t-BuCl and *t*-BuOH. It has been found from calorimetric experiments that SbCl_5 does not interact with HCl in 1,2-dichloroethane solution to give any measurable enthalpy change.⁵ The interaction between SbCl_5 and HCl in an inert solvent is assumed to be negligible. The enthalpy change, ΔH_4 , for the hypothetical reaction (4) can thus be found by subtracting either (a): the enthalpy of solution of *t*-BuCl from ΔH_1 or (b): the enthalpy of solution of SbCl_5 (-1.80 kJ \cdot mol $^{-1}$)⁶ from ΔH_2 :

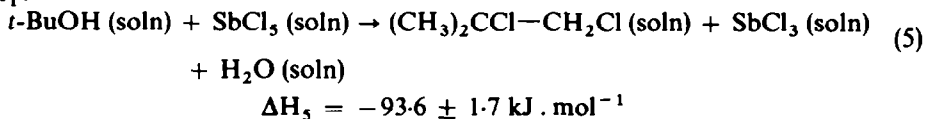


$$(a) \quad \Delta H_4 = -72.4 \pm 2.0 \text{ kJ} \cdot \text{mol}^{-1}$$

$$(b) \quad \Delta H_4 = -72.0 \pm 0.2 \text{ kJ} \cdot \text{mol}^{-1}$$

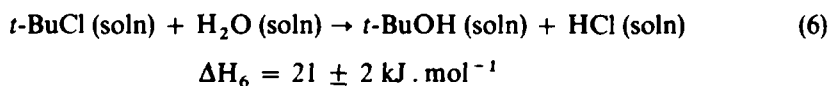
The enthalpy of adduct formation between H_2O and SbCl_5 has been redetermined and a value of (-77.8 ± 1.5) kJ \cdot mol $^{-1}$ was found¹⁰(*cf.* Ref. 9). The enthalpy change, ΔH_5 , for the hypothetical reaction (5) can be found by subtracting the enthalpy of

formation of the $\text{SbCl}_5 \cdot \text{H}_2\text{O}$ adduct and the enthalpy of solution of *t*-BuOH from ΔH_1 :



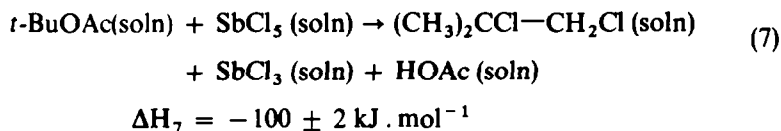
This value is compatible with the value of $-94 \pm 2 \text{ kJ} \cdot \text{mol}^{-1}$ that can be derived from ΔH_2 by subtracting the enthalpy of solution of SbCl_5 and taking into account the interaction between SbCl_3 and H_2O . The enthalpy change for the latter interaction is difficult to estimate as the stability constant is unknown but will not exceed $-2.9 \text{ kJ} \cdot \text{mol}^{-1}$ which is the value found from the dissolution experiments.

Subtracting reaction (5) from (4) gives the following reaction:



It can be assumed that ΔH_6 approximates to the enthalpy change in gaseous state as 1,2-dichloroethane is an inert solvent.* From enthalpy of formation values given in Ref. 8 the enthalpy change for reaction (6) in gaseous phase is calculated to be $20.5 \pm 2.4 \text{ kJ} \cdot \text{mol}^{-1}$. The good agreement shows that the interpretation of the calorimetric experiments is thermochemically sound. It can be concluded that *t*-BuCl and *t*-BuOH are chlorinated instantaneously and quantitatively by SbCl_5 in dilute solution according to reactions (4) and (5), respectively.

BuOAc. In the calorimetric experiments with SbCl_5 in excess the final solution contained about $0.012 \text{ mol} \cdot \text{l}^{-1}$ of the $\text{SbCl}_5\text{-HOAc}$ adduct. The adduct is partly associated in solution, most likely as the dimer, and the apparent enthalpy of adduct formation at this concentration is estimated from calorimetric measurements to be about $-46 \pm 2 \text{ kJ} \cdot \text{mol}^{-1}$.⁷ Subtracting the enthalpy of formation of the acetic acid adduct and enthalpy of solution of *t*-BuOAc ($-0.5 \pm 0.1 \text{ kJ} \cdot \text{mol}^{-1}$)¹ from ΔH_1 the enthalpy change, ΔH_7 for the hypothetical reaction (7) is found.



The interaction between SbCl_3 and HOAc in this concentration region was found from calorimetric measurements to be negligible.

The results of the calorimetric experiments with *t*-BuOAc in excess show that rapid chlorination does not take place under these conditions. The enthalpy change of the first rapid step of the complex reaction is only about half the value expected for the chlorination reaction and is more of the magnitude of SbCl_5 -ester adduct formation.⁹

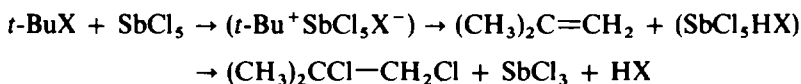
DISCUSSION

The readiness of chlorination of *t*-Bu compounds by SbCl_5 depends on the nature of the atom bound to the *t*-Bu group. *t*-Bu ketones, dineopentyl ketone and methyl and ethyl pivalate interact with SbCl_5 to give electron donor-acceptor adducts.⁹

* Due to lack of knowledge of the enthalpy of solution of water in 1,2-dichloroethane, ΔH_6 cannot be recalculated to refer to the reaction with reactants and reaction products in standard states.

The enthalpies of adduct formation in 1,2-dichloroethane solution are between -50 to -70 $\text{kJ} \cdot \text{mol}^{-1}$. The new bond in the adduct is formed by donation of one lone electron pair at the carbonyl oxygen to a vacant orbital at the Sb atom. In these donors the *t*-Bu group is bound to a carbon atom possessing no lone electron pairs that can interact with a Lewis acid.

t-BuCl and *t*-BuOH are instantaneously chlorinated in dilute solution to give 1,2-dichloro-2-methylpropane. In these compounds the atom bound to the *t*-Bu group possesses lone electron pairs. The chlorination can be assumed to proceed via attack of SbCl_5 at the atom next to the *t*-Bu group and formation of *t*-Bu cation. The hypothetical reaction path could be as follows:



t-BuOAc contains two oxygen atoms capable of interaction with SbCl_5 . In donor-acceptor adducts between esters and Lewis acids the carbonyl oxygen atom functions as donor atom.¹⁰ In solutions containing *t*-BuOAc in excess the first step is likely to be adduct formation with carbonyl oxygen as the donor atom. The SbCl_5 moiety would be stabilized in the adduct. An example of the reduced chlorination power of SbCl_5 under conditions where an SbCl_5 adduct is formed is given in Ref. 11. The authors were able to study the hydrogen exchange between *t*-BuCl and deuterioacetic acid in the presence of SbCl_5 and found indications of only slow irreversible reactions. Judging from other alkyl carboxylate- SbCl_5 systems the stability constant of the *t*-BuOAc adduct can be expected to be large and the equilibrium concentration in solution of SbCl_5 will thus be small.⁹ The different rates of chlorination found for *t*-BuOAc when SbCl_5 was either in excess or in deficiency can be interpreted as being due to differences in concentration of unbound SbCl_5 free to interact with the ether oxygen atom.

In an NMR study of the formation of alkyl carbonium ions Olah *et al.*¹² reported that stable solutions of *e.g.* *t*-BuCl in liquid Lewis acid halides as TiCl_4 and SbCl_5 could be prepared at low temperature. PMR chemical shifts were reported to indicate only weak donor-acceptor interaction between the components. While their results for the *t*-BuCl- TiCl_4 system are concordant with results of the calorimetric experiments their statement about the *t*-BuCl- SbCl_5 system is not consistent with results reported in the present paper or in Ref. 2. Meyer and Müller² added SbCl_5 to *t*-BuCl slowly under cooling in molar ratio 1:1. A vigorous reaction took place and they isolated 1,2-dichloro-2-methylpropane. In the present study *t*-BuCl was frozen out on an excess of solid SbCl_5 . As soon as the reactants started to melt gas evolution took place. A clear although miscoloured solution was obtained which did not change upon standing. PMR spectra indicated the following secondary reaction to take place:



This reaction also takes place in dilute solution.

EXPERIMENTAL

Materials

t-BuOH (Eastman) was dried with Molecular Sieves 4A and distilled at atmospheric pressure on a Nester-Faust Auto Annular Spinning Band Distillation Column. The purity was checked by analytical GLC using dioctylphthalate and Carbowax as stationary phases and was judged to be better than 99.7 percent. The

H₂O content of the sample was checked separately by GC¹³ and found to be less than 0.02 percent by volume. No impurities could be detected by analytical GLC in the sample of *t*-BuCl (2-chloro-2-methylpropane) kindly provided by Dr. I. Wadsö at this laboratory. The H₂O content of the sample was less than 5 ppm.

The sample of *t*-BuOAc used in the calorimetric measurements is described in Ref. 1. Another sample used in the PMR experiments was found to be better than 99.5 percent pure as judged from analytical GLC using dioctylphthalate as stationary phase. HOAc see Ref. 14. 1,2-Dichloroethane (Schuckardt) was used without further treatment. 1,2-Dichloroethane (Fisher Certified Reagent) was fractionally distilled and stored with dust free beads of Molecular Sieves 4A. No impurities could be detected by analytical GLC using a dioctylphthalate column. The H₂O content of the solvent as determined by GC¹³ was about 10 ppm (by volume). CHCl₃ of analytical grade was treated with Molecular Sieves 4A to remove EtOH and H₂O. No impurities could be detected in PMR spectrum of the sample. SbCl₃ was treated as given in Ref. 15. In some of the experiments Merck's SbCl₃ of chromatographic grade was used without further treatment. SbCl₃ (BDH 'Analar') certified to be better than 99.5 percent pure was resublimated before use. TiCl₄ (Schuckardt) of analytical grade was not further purified.

The samples of the SbCl₃, SbCl₃ and TiCl₄ were handled in an atmosphere of dry N₂. Samples for the PMR analyses were prepared by mixing under cooling 5 ml portions of stock solutions of the reactants. After the sample had reached room temperature an appropriate amount was transferred to PMR tubes. The spectra were recorded at 37°C.

Apparatus

Calorimetric equipment see Ref. 14. The PMR spectra were recorded on a Varian A60 spectrometer.

Calorimetric Procedure

The calorimeter was charged with 1,2-dichloroethane and an appropriate amount of one of the reactants was added. After equilibration the reaction was started by breaking the thin walled glass ampoule containing the second reactant. In all experiments the reaction periods were short and the corrected thermistor resistance values (R_i and R_f) were evaluated by extrapolating the fore and after periods to the time corresponding to 0.63 of the resistance change (Dickinson's extrapolation method). For the electrical calibrations, which were performed on the systems before the reaction took place, extrapolation were taken to the time corresponding to 0.50 of the temperature change. The expression $R_i - R_f/R_i + R_f$ was used as being proportional to the temperature change.⁴

The results of the calorimetric experiments refer to the isothermal process at 25°C and to true mass. The experiments with *t*-BuOH (m.p. 25.5°C) do, however, refer to 27°C.

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