

Adducts between Antimony Pentachloride and Various Ketones. A Calorimetric Study

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Enthalpies of formation of a number of donor-acceptor adducts have been determined with both reactants and reaction products in ethylene chloride solution. With antimony pentachloride as acceptor, the heats of formation ($-\Delta H$ kcal-mole⁻¹) of the addition compounds of the following ketones were found as follows: methyl propyl ketone (17.50); diisobutyl ketone (16.38); di-neopentyl ketone (15.00); *tert*-butyl isopropyl ketone (11.60); di-*tert*-butyl ketone (9.6); *tert*-butyl neopentyl ketone (11.78) and cyclohexanone (17.79).

The stability constants were determined for the adducts of the following ketones and the values obtained, in units of l-mole⁻¹, are given within brackets: *tert*-butyl isopropyl ketone (3700); di-*tert*-butyl ketone (330) and *tert*-butyl neopentyl ketone (265).

The shifts in carbonyl stretching frequency caused by adduct formation have been determined for diethyl ketone and cyclohexanone. The values found were 112 and 106 cm⁻¹, respectively.

In previous communications,^{1,2} enthalpies of formation of adducts between antimony pentachloride and a number of ketones have been reported. The ketones were chosen to show the influence of methyl substituents in a position α to the carbonyl group. This paper gives data of some β -methyl substituted ketones together with the enthalpy value of the cyclohexanone adduct. Stability constants have been determined for adduct formation of three sterically crowded ketones.

EXPERIMENTAL

Materials. Ethylene chloride (Fisher Certified Reagent) was distilled (*cf.* Ref. 3) shortly before use.

Antimony pentachloride was treated as described in Ref. 4. In the experiments with 0.3 M solutions Merck's antimony pentachloride for chromatography was used without further treatment.

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The purity of the following ketones has been checked by analytical GLC using polyethyleneglycol on Chromosorb P. Unless stated otherwise the samples were free from impurity.

Methyl propyl ketone (BDH) was dried with Drierite and fractionally distilled; n_D^{25} 1.3880, d_4^{25} 0.8016.

Diisobutyl ketone (Fluka) was fractionally distilled and the main fraction further purified using preparative GLC (Wilkins Autoprep, Carbowax 20 M on Chromosorb W). The sample was dried with CaH_2 before use; n_D^{25} 1.4102, d_4^{25} 0.8021.

Cyclohexanone (Riedel—de Haën) was fractionally distilled under reduced pressure. The sample was shown to be free from impurities (*e.g.*, no cyclohexanol could be detected) by analytical GLC using in addition to the polyethyleneglycol column dioktylphthalate as stationary phase on Celite. Freshly regenerated micro sieves were used to dry the sample. The water content of this sample was checked by gas chromatography using a Porapak Q column^{5,6} and was found to be less than 0.01 % by volume. The difference between the literature value of the density, d_4^{25} 0.94010,⁷ and the value found in this investigation cannot be explained; n_D^{25} 1.4510 d_4^{25} 0.9467.

Diethyl ketone was the same sample as used in Ref. 2.

The following ketones were obtained from Dr. L. Ebersson, Dept. of Chemistry, Lund University, and the samples were purified, using GLC (Wilkins Autoprep, Carbowax 20 M on Chromosorb W), by Dr. P. Sellers at this Thermochemistry Laboratory. Di-*tert*-butyl ketone and, especially, dioneopentyl ketone proved to be difficult to purify. It was only by a very careful manual operation with 0.07 ml injections that a sample of dioneopentyl ketone of satisfactory purity could be obtained.

All samples were dried with CaH_2 before use. For data on *tert*-butyl isopropyl ketone, di-*tert*-butyl ketone and *tert*-butyl neopentyl ketone see Ref. 8. The purity of dioneopentyl ketone was shown by analytical GLC to be 99 ± 1 %. Mass spectrometric analysis confirmed the identity of the sample; n_D^{25} 1.4169.

Apparatus. Calorimetric and infrared spectroscopic equipment, see Ref. 9. The mass spectrogram was recorded on an LKB 9000 Gas Chromatograph-Mass Spectrometer.

Calibration, see Ref. 3. The calibration time was 60–150 sec.

Calorimetric procedure. The standard calorimetric procedure to determine enthalpies of adduct formation has been described elsewhere,⁸ as have the simultaneous determinations of enthalpies and stability constants of adduct formation.⁹ The initial and final resistance values were obtained graphically. In the determinations with di-*tert* butyl ketone, dioneopentyl ketone, and cyclohexanone the expression $(\log R_i - \log R_f)/\log R_i \times \log R_f$ was used and in all other determinations $(R_i - R_f)/(R_i + R_f)$ was employed. Both these quantities are proportional to ΔT .¹⁰

Infrared measurements were performed as described in Ref. 9.

Corrections to standard states, see Ref. 3.

Units of measurements. The results of the calorimetric experiments are expressed in terms of the defined calorie equal to 4.1840 abs.joules. Given thermodynamic data refer to the isothermal process at 25°C and to the true mass. The molecular weights were computed from the 1961 *Table of Atomic Weights*.¹¹

RESULTS

The results of the heat of reaction measurements, where conversion to adduct was complete, are summarized in Table 1. The first column identifies the donor together with a sum correction p (in cal) compensating for small heat effects arising from incompletely filled ampoules.¹⁰ Columns 2 and 3 give the amounts of donor and acceptor and column 4 the corrected amount of heat evolved. The last column gives the molar enthalpy change.

In cases where the conversion to adduct was incomplete in the concentration region used, it was possible to determine ΔH and K simultaneously for the adduct formation by measuring the heat evolved with varying concentrations of the reactants. The following equation has been derived for the rela-

Table 1. Heat of reaction measurements performed in ethylene chloride solution containing excess SbCl_5 as acceptor.

Donor	mmole	g SbCl_5	q cal	$-\Delta H$ kcal/mole
2-Pentanone $p = 0.02$	1.029	1.32	18.29	17.77
	1.044	1.40	18.62	17.83
	1.718	1.54	30.47	17.74
	1.877	1.49	33.38	17.78
				17.78 \pm 0.02
2,6-Dimethyl-4-heptanone $p = 0.02$	1.559	1.50	24.92	15.98
	1.896	1.52	30.35	16.01
	2.182	1.49	34.94	16.01
	2.257	1.49	36.09	15.99
				16.00 \pm 0.01
2,2,6,6-Tetramethyl-4-heptanone $p = 0.03$	0.798	0.96	11.42	14.32
	1.110	1.30	15.91	14.34
	1.297	1.55	18.60	14.34
				14.33 \pm 0.01
Cyclohexanone $p = 0.03$	1.138	0.98	20.91	18.38
	1.173	1.05	21.54	18.36
	1.185	1.30	21.81	18.40
	1.690	1.14	31.06	18.38
				18.38 \pm 0.01

relationship between the enthalpy of formation, ΔH , and the stability constant, K , of 1:1 adducts:⁹

$$(-\Delta H)^2 + \Delta H \cdot h \left(1 + \frac{d}{a} + \frac{V}{a \cdot K} \right) + \frac{h^2 \cdot d}{a} = 0 \quad (1)$$

d and a are the amounts of donor and acceptor and V the total volume of solution. h is the heat evolved, corrected for heat of solution, in an experiment where an unknown amount of adduct is formed.

The results of the calorimetric experiments are summarized in Table 2. The first column identifies the donor and columns 2 and 3 give the amount of donor and acceptor, respectively. Column 4 gives the heat evolved in an experiment, corrected for small heat effects due to incompletely filled ampoules.¹⁰ The last column shows the heat evolved per mmole of donor in an experiment where an unknown amount of adduct is formed. The amount of SbCl_5 has been corrected for the presence of a small quantity of water in the ethylene chloride used. The amount of water was determined as described in Ref. 12 and was found to be 0.16 ± 0.05 mmole/charge in the measurements with $t\text{-Bu}(\text{i-Pr})\text{CO}$ and 0.22 ± 0.05 and 0.40 ± 0.10 mmole/charge in the measurements with $t\text{-Bu}_2\text{CO}$ and $t\text{-Bu}(\text{neoPe})\text{CO}$, respectively.

The ΔH and K values of *tert*-butyl isopropyl ketone and *tert*-butyl neopentyl ketone were evaluated by minimizing the square of the error sum of

Table 2. Heat of reaction measurements in ethylene chloride solution where an unknown amount of adduct was formed.

Donor	mmole	mmole SbCl ₅	q cal	h cal/mmole
2,2,4-Trimethyl-3-pentanone	2.074	2.41	22.68	10.94
	2.284	2.67	25.04	10.96
	1.694	3.19	19.13	11.29
	0.776	3.23	8.90	11.48
	0.999	4.48	11.50	11.51
	1.000	6.50	11.58	11.58
	1.103	8.51	12.76	11.57
	1.084	9.45	12.48	11.52
2,2,4,4-Tetramethyl-3-pentanone	1.988	2.58	14.55	7.53
	1.752	2.61	13.01	7.64
	0.875	3.94	7.48	8.75
	0.841	4.73	7.35	8.95
	0.924	7.06	8.50	9.41
	1.120	10.65	11.77	9.85
	0.846	33.2	8.86	10.70
2,2,5,5-Tetramethyl-3-hexanone	0.581	2.53	5.49	10.01
	0.828	2.89	7.94	10.13
	0.466	3.12	4.39	10.01
	0.517	32.6	5.71	11.61
	1.346	32.7	15.03	11.69
	1.205	33.4	13.39	11.66

eqn. 1 for a network of ΔH and K values.⁹ The derived enthalpy and stability constant values were 11.60 ± 0.01 ; 3700 ± 110 [*t*-Bu(*i*-Pr)CO] and 11.78 ± 0.08 kcal·mole⁻¹; 265 ± 20 l·mole⁻¹ [*t*-Bu(*neo*Pe)CO], respectively. The error limits, expressed as standard deviations of the means have been estimated as described in Ref. 9. The ΔH -value of *t*-Bu(*i*-Pr)CO found in this investigation is in satisfactory agreement with the earlier reported value² -11.34 kcal·mole⁻¹ as the latter refers to about 98 % conversion to adduct.

For di-*tert*-butyl ketone it was not possible to find a pair of values of ΔH and K which satisfied the equation system obtained when data from the different experiments were inserted in eqn. 1. When, *e.g.*, data from experiment No. 3 in Table 2 were combined with data from the other six experiments a series of ΔH and K values were found where the $-\Delta H$ values increased from 9.46 kcal/mole (expt. 1) to 10.97 (expt. 7) and the K values decreased from 402 to 124 l·mole⁻¹ with increasing SbCl₅ concentration. It was concluded that a side reaction depending on the amount of excess SbCl₅ took place at the same time as the adduct formation. The main periods in the calorimetric experiments were only slightly longer than usual (about 5 min instead of 4). The heat leakage constant values were 20 % low in the experiments with low concentration of SbCl₅ and 50 % low in the experiment with 0.33 M SbCl₅. The heat evolution in the after period was, however, small (of the magnitude 20–50 microcal·min⁻¹) and did not influence the determination of the heat evolved in the main period as graphical extrapolation of the initial and final

resistance values was used.¹⁰ By inserting data from the four first experiments in Table 2 and solving the equation systems obtained the following values were derived: $-\Delta H = 9.64 \pm 0.07$ kcal·mole⁻¹ and $K = 330 \pm 26$ l·mole⁻¹. The influence of a side reaction on these values would give a high value of $-\Delta H$ and a low value of K . The errors are estimated to be 0.2 kcal·mole⁻¹ in ΔH and 50 l·mole⁻¹ in K .

The enthalpy of adduct formation of di-*tert*-butyl ketone found in this investigation differs from that given in Ref. 2 (-10.30 kcal·mole⁻¹). After publication it was discovered by Dr. Sellers that the sample used in Ref. 2 was only about 95 % pure.

The heat of solution measurements (Table 3) were performed in pure ethylene chloride. Values for heat of solution of *tert*-butyl isopropyl ketone and di-*tert*-butyl ketone were taken from Ref. 2.

Summaries of the determinations are given in Tables 4 and 5. In Table 4 the first column shows the formula of the donor and the second the heat of reaction between liquid donor and SbCl₅ in ethylene chloride solution. The heat of solution is given in the third column and the fourth column states the calculated value of the enthalpy change for the reaction with both reactants and reaction product in ethylene chloride solution. The value for dioneopentyl ketone has been corrected for the impurity content of about 1 %. A sample containing about 5 % of the same impurity gave a heat of reaction ($-\Delta H_1$) of 14.75 kcal·mole⁻¹. The error limit includes the estimated uncertainty in this correction. Previously reported data for three ketones have been included in Table 4.

Table 3. Heat of solution measurements of various donors in ethylene chloride.

Donor	mmole	<i>q</i> cal	$-\Delta H$ kcal/ mole
2-Pentanone <i>p</i> = 0.02	1.443	0.41	0.28
	1.924	0.54	0.28
	2.604	0.73	0.28
			0.28 ± 0.00
2,2,5,5-Tetramethyl-3-hexanone <i>p</i> = 0.02	1.648	-0.85	-0.52
	1.992	-1.02	-0.51
			-0.52 ± 0.01
2,6-Dimethyl-4-heptanone <i>p</i> = 0.02	2.116	-0.80	-0.38
	3.023	-1.12	-0.37
			-0.38 ± 0.01
2,2,6,6-Tetramethyl-4-heptanone <i>p</i> = 0.02	2.097	-1.58	-0.75
	2.478	-1.84	-0.74
			-0.75 ± 0.01
Cyclohexanone <i>p</i> = 0.03	1.862	1.09	0.59
	2.134	1.26	0.59
			0.59 ± 0.00

Table 4. Enthalpy changes accompanying the formation of adducts between SbCl_5 and various ketones in ethylene chloride solution.

Donor	$-\Delta H_1$ kcal-mole $^{-1}$	$-\Delta H_2$ kcal-mole $^{-1}$	$-\Delta H$ kcal-mole $^{-1}$
Me_2CO^a	17.39	0.36	17.03 ± 0.04
$\text{Me}(\text{Et})\text{CO}^b$	17.80	0.37	17.43 ± 0.03
$\text{Me}(\text{n-Pr})\text{CO}$	17.78	0.28	17.50 ± 0.02
Et_2CO^b	16.80	0.27	16.53 ± 0.03
$i\text{-Bu}_2\text{CO}$	16.00	-0.38	16.38 ± 0.02
neoPe_2CO	14.33	-0.75	15.00 ± 0.10
$\text{CH}_2-(\text{CH}_2)_4\text{-CO}$	18.38	0.59	17.79 ± 0.01

^a From Ref. 3.

^b From Ref. 2.

Table 5. Thermodynamic quantities involved in the formation of adducts between SbCl_5 and various ketones in ethylene chloride solution.

Donor	$-\Delta H$ kcal-mole $^{-1}$	K l-mole $^{-1}$	$-\Delta G$ kcal-mole $^{-1}$ ^a	$-\Delta S$ e.u.
$t\text{-Bu}(i\text{-Pr})\text{CO}$	11.60 ± 0.03	3700 ± 300	2.97 ± 0.05	28.9 ± 0.2
$t\text{-Bu}_2\text{CO}$	$9.6 \begin{smallmatrix} +0.1 \\ -0.3 \end{smallmatrix}$	$330 \begin{smallmatrix} +80 \\ -30 \end{smallmatrix}$	$1.54 \begin{smallmatrix} +0.13 \\ -0.05 \end{smallmatrix}$	$27.0 \begin{smallmatrix} +0.4 \\ -1.1 \end{smallmatrix}$
$t\text{-Bu}(\text{neoPe})\text{CO}$	11.78 ± 0.10	265 ± 35	1.41 ± 0.08	34.8 ± 0.4

^a From K in atm $^{-1}$.

In Table 5 the first column shows the formula of the donor. Columns 2 and 3 give the enthalpy change for adduct formation and stability constant of the adduct, respectively. The calculated values of the free energy and entropy changes are given in columns 4 and 5. These thermodynamic quantities refer to the addition reaction with both reactants and reaction product in ethylene chloride solution. The error limits given for the enthalpy and stability constant values include allowance for uncertainty in the water content of the calorimetric liquid.

Table 6. Infrared spectra measurements performed on ethylene chloride solutions of free donors and of SbCl_5 adducts.

Donor	Carbonyl stretching frequency cm^{-1}		shift cm^{-1}
	free donor	adduct	
$(\text{C}_2\text{H}_5)_2\text{CO}$	1702	1590	112 ± 5
$\text{CH}_2-(\text{CH}_2)_4\text{-CO}$	1698	1592	106 ± 5

The infrared spectra measurements were performed using ethylene chloride solutions 0.02 M in ketone and 0.05 M in SbCl_5 . The results of the infrared measurements are given in Table 6. The first column shows the donor and columns 2 and 3 give the carbonyl stretching frequencies of the free donor and of the adduct, respectively. The last column indicates the shift in frequency caused by adduct formation.

DISCUSSION

Enthalpies of adduct formation between SbCl_5 and ketones of general formula $(\text{CH}_3)_i\text{CH}_3\text{-}_i\text{COCH}_3\text{-}_j(\text{CH}_3)_j$ ($i, j = 0, 1, 2, \text{ or } 3$) have been reported earlier and the effects of α -methyl substitution have been discussed in terms of inductive and steric effects.^{1,2} A positive inductive effect of the methyl group was found only when a methyl group replaced a hydrogen atom in acetone to give methyl ethyl ketone. The difference between the $-\Delta H$ -values was observed to be $0.4 \text{ kcal}\cdot\text{mole}^{-1}$. Conversely, diethyl ketone gave a $-\Delta H$ value $0.5 \text{ kcal}\cdot\text{mole}^{-1}$ lower than acetone. It is interesting to compare these values with that for cyclohexanone which is $1.3 \text{ kcal}\cdot\text{mole}^{-1}$ higher than diethyl ketone. The inductive effect of the alkyl groups are presumably the same in diethyl ketone and cyclohexanone. The higher $-\Delta H$ value of the cyclic ketone is probably due to the fact that in the ring compound the alkyl groups are held back from the carbonyl group in a rigid position and it is possible for the oxygen atom to coordinate with the acceptor with a minimum of steric hindrance.

The carbonyl stretching frequency shifts caused by adduct formation were, within the limits of experimental error, the same for diethyl ketone (112 cm^{-1}) and cyclohexanone (106). These frequency shifts may be compared with the shift of 160 cm^{-1} found when ethyl acetate acts as donor.⁹ A similar difference between frequency shifts for alkyl ketone and ester adducts was found by Lappert¹³ who studied the boron trifluoride adducts of acetone (shift of 70 cm^{-1}) and ethyl acetate (119 cm^{-1}). The enthalpy of formation of the SbCl_5 -ethyl acetate adduct was -17.08 kcal/mole .³ If the enthalpy of adduct formation is taken as a measure of donor strength it can be concluded that the frequency shifts do not show a simple correlation with donor strength (*cf.* Ref. 14).

The effects on the enthalpies of adduct formation of methyl substitution in a position β - to the carbonyl group are less pronounced than the effects of α -substitution. The difference between the $-\Delta H$ values of acetone and di-isopropyl ketone ($16.20 \text{ kcal}\cdot\text{mole}^{-1}$)² is $0.8 \text{ kcal}\cdot\text{mole}^{-1}$, while the difference between diethyl ketone and diisobutyl ketone is 0.2 . The $-\Delta H$ value of di-*tert*-butyl ketone has been measured as $9.6 \text{ kcal}\cdot\text{mole}^{-1}$ whereas dineopentyl ketone, in which the methyl groups are attached to β -carbon atoms, gave an enthalpy of adduct formation value of $-15.00 \text{ kcal}\cdot\text{mole}^{-1}$.

The observed value of the entropy change accompanying the adduct formation of *tert*-butyl isopropyl ketone (-28.9 e.u.) is significantly different from the value found for *tert*-butyl neopentyl ketone adduct (-34.8 e.u.) although the enthalpy values are almost the same. The reason may be that the entropy value of the *tert*-butyl neopentyl ketone adduct reflects a larger change between

free and bounded ketone. The alkyl groups interlock rather more than when the *tert*-butyl isopropyl ketone adduct is formed. In the crowded molecule of *tert*-butyl isopropyl ketone and, to a larger extent, in the di-*tert*-butyl ketone, the alkyl groups in the unbounded ketone are restricted to a narrow range of positions. In the di-*tert*-butyl ketone adduct it is possible that the weaker interaction between donor and acceptor ($-\Delta H = 9.6 \text{ kcal}\cdot\text{mole}^{-1}$) could have an influence on the entropy change and partly be the reason for the even lower entropy of formation (-27 e.u.) of this adduct. It is noticeable that the ΔS value of the *tert*-butyl neopentyl ketone adduct is almost the same as when ethyl pivalate is donor ($-\Delta H = 13.03 \text{ kcal}\cdot\text{mole}^{-1}$; $-\Delta S = 34.7 \text{ e.u.}$).⁹

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REFERENCES

1. Olofsson, G. *Acta Chem. Scand.* **18** (1964) 11.
2. Olofsson, G. *Acta Chem. Scand.* **19** (1965) 2155.
3. Olofsson, G., Lindqvist, I. and Sunner, S. *Acta Chem. Scand.* **17** (1963) 259.
4. Olofsson, G. *Acta Chem. Scand.* **21** (1967) 93.
5. Hollis, O. L. and Hayes, W. V. *J. Gas Chromatog.* **4** (1966) 235.
6. Sellers, P. *To be published.*
7. Sellers, P. and Sunner, S. *Acta Chem. Scand.* **16** (1962) 46.
8. Sellers, P. *To be published.*
9. Olofsson, G. *Acta Chem. Scand.* **21** (1967) 1892.
10. Wadsö, I. *Sci. Tools* **13** (1966) 33.
11. Cameron, A. E. and Wichers, E. *J. Am. Chem. Soc.* **84** (1962) 4175.
12. Olofsson, G. *Acta Chem. Scand.* **21** (1967) 1887.
13. Lappert, M. F. *J. Chem. Soc.* **1961** 817.
14. Olofsson, G. *Acta Chem. Scand.* **21** (1967) 1114.

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