Heats of Formation of Adducts between Antimony

Pentachloride and Some Ketones

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Heats of formation of a number of electron donor-acceptor adducts have been determined with both reactants and reaction products in 1,2-dichloroethane solution. Antimony pentachloride was the acceptor and the following ketones were donors: the obtained heat of formation values in kcal. mole^{-1} are given within brackets: diethyl ketone (16.53), ethyl isopropyl ketone (16.16), diisopropyl ketone (16.20), *tert*-butyl ethyl ketone (14.58), *tert*-butyl isopropyl ketone (11.34), di-*tert*-butyl ketone (10.30). The data obtained have been discussed.

In previous communications [1,2] the determinations of the enthalpy of adduct formation between four ketones and antimony pentachloride in ethylene chloride solution have been reported. This paper gives further data on six ketones chosen to illustrate the effect of bulky substituents attached to the carbonyl group.

EXPERIMENTAL **

Materials. Ethylene chloride and *antimony pentachloride* were treated as given in Ref. 1. *Diethyl ketone* (Fluka) and *ethyl isopropyl ketone* (Fluka) were treated with Drierite and then distilled. The purity was checked by GLC (Apeizon L on Chromosorb P). Diethyl ketone: b.p. 102.0° at 760 mm Hg, n_D^{25} 1.3900, d_4^{25} 0.8093; ethyl isopropyl ketone: b.p. 112.5° at 746 mm Hg, n_D^{25} 1.3952, d_4^{25} 0.8063.

The following ketones were obtained from Dr. L. Eberson, Dept. of Chemistry, Lund University. Samples, purified by preparative GLC, were supplied by Dr. P. Sellers at the Thermochemistry Laboratory. The purities were checked by analytical GLC using Apeizon L on Chromosorb P as stationary phase. *tert*-Butyl ethyl ketone: n_D^{25} 1.4028, d_4^{25} 0.8084; diisopropyl ketone: n_D^{25} 1.3976, d_4^{25} 0.7985; *tert*-butyl isopropyl ketone: n_D^{25} 1.4040, d_4^{25} 0.8026; di-*tert*-butyl ketone: n_D^{25} 1.4173, d_4^{25} 0.8207.

Units of measurements. The results of the calorimetric experiments are expressed in terms of the defined calorie, equal to 4.1840 abs. joules, and refer to the isothermal process at 25° and to the true mass. The molecular weights were computed from the 1961 table of atomic weights.[3]

** *Apparatus, Calibration, Calorimetric procedure* and *Correction to standard states.* See Ref. 1.

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

Donor	mmole	g $SbCl_5$	$10^4 \times \log R_i/R_f$	$-\Delta H$ kcal/mole
3-Pentanone (I)	1.168	1.05	47.99	16.82
$q = -0.01$	1.584	1.20	64.81	16.77
	2.101	1.57	85.64	16.74
	3.072	1.49	126.43	16.91
(II)	1.320	1.10	55.04	16.74
				16.80 $\pm$ 0.03
2-Methyl-3-pentanone (I)	1.193	1.08	47.57	16.34
$q = -0.01$	1.403	1.22	56.18	16.41
	2.154	1.30	85.66	16.32
	2.911	1.65	115.76	16.30
				16.34 $\pm$ 0.03
2,4-Dimethyl-3-pentanone (I)	1.155	1.05	45.85	16.27
$q = 0.00$	1.335	1.16	52.94	16.26
	1.997	1.22	78.85	16.20
	2.116	1.24	83.52	16.20
	2.416	1.39	95.63	16.26
	2.507	1.50	99.33	16.28
				16.24 $\pm$ 0.02
2,2-Dimethyl-3-pentanone (I)	0.967	1.28	34.45	14.61
$q = 0.00$	1.122	1.31	40.07	14.65
	1.203	1.11	42.88	14.61
	1.418	1.16	50.41	14.58
	2.218	1.48	78.87	14.62
				14.61 $\pm$ 0.01
2,2,4-Trimethyl- -3-pentanone (III)	0.826	1.05	26.44	11.37
$q = 0.00$	1.206	0.99	38.63	11.33
	2.234	1.22	71.30	11.32
	2.251	1.25	71.67	11.29
				11.33 $\pm$ 0.02
2,2,4,4-Tetramethyl- -3-pentanone (I)	0.960	1.05	23.60	10.08
$q = 0.00$	1.609	1.16	39.48	10.07
	1.671	1.11	40.90	10.04
	2.352	1.26	57.44	10.03
				10.06 $\pm$ 0.02

RESULTS

The experimental results are summarized in Tables 1 and 2. Three different systems were used, I, II, and III, with heat equivalents in cal per unit of log R_i/R_f, 4095 $\pm$ 2, 4012 $\pm$ 2 and 3535 $\pm$ 2, respectively. In the heat of reaction measurements (Table 1) the first column gives the name of the donor together with a sum correction q, compensating for a number of small heat effects.[1] Columns 2 and 3 give the amounts of donor and acceptor. The $SbCl_5$ was added in excess prior to the experiments to take care of traces of water inside

Table 2. Heat of solution measurements of the different donors in ethylene chloride.

Donor	mmole	$10^4 \times \log R_i/R_f$	$-\Delta H$ kcal/mole
3-Pentanone (II)	2.186	1.48	0.27
$q = 0.01$	2.549	1.73	0.27
			0.27 ± 0.00
2-Methyl-3-pentanone (I)	2.522	1.09	0.18
$q = 0.01$	3.138	1.38	0.18
			0.18 ± 0.00
2,4-Dimethyl-3-pentanone (I)	2.149	0.14	0.04
$q = 0.02$	2.900	0.20	0.03
			0.04 ± 0.01
2,2-Dimethyl-3-pentanone (I)	1.482	0.05	0.03
$q = 0.02$	2.327	0.10	0.03
			0.03 ± 0.00
2,2,4-Trimethyl-3-pentanone (I)	2.584	−0.09	−0.01
$q = 0.02$	2.648	−0.05	0.00
			−0.01 ± 0.01
2,2,4,4-Tetramethyl-3-pentanone (III)	1.196	−0.78	−0.24
$q = 0.02$	2.251	−1.40	−0.23
			−0.24 ± 0.01

the calorimeter and in the solvent. Column 4 gives the corrected temperature rise expressed in units of $10^4 \times \log R_i/R_f$, where R_i and R_f are the extrapolated initial and final thermistor resistances. The last column gives the molar enthalpy change. The heat of solution experiments (Table 2) were performed in pure ethylene chloride. The data are summarized in Table 3 together with the calculated values of the enthalpy change for the reaction with both reactants and reaction product in solution. Previously reported data for ketones have been included in Table 3.

Table 3. Enthalpy changes accompanying the formation of adducts between SbCl₅ and different ketones in ethylene chloride solution.

Donor	$-\Delta H_1$ kcal.mole⁻¹	$-\Delta H_2$ kcal.mole⁻¹	$-\Delta H$ kcal.mole⁻¹
Me₂CO *	17.39	0.36	17.03 ± 0.04
Me(Et)CO **	17.80	0.37	17.43 ± 0.03
Me(*i*-Pr)CO **	17.41	0.34	17.08 ± 0.03
Me(*t*-Bu)CO **	17.19	0.24	16.95 ± 0.03
Et₂CO	16.80	0.27	16.53 ± 0.03
Et(*i*-Pr)CO	16.34	0.18	16.16 ± 0.03
i-Pr₂CO	16.24	0.04	16.20 ± 0.03
Et(*t*-Bu)CO	14.61	0.03	14.58 ± 0.01
i-Pr(*t*-Bu)CO	11.33	−0.01	11.34 ± 0.03
t-Bu₂CO	10.06	−0.24	10.30 ± 0.03

* From Ref. 1.
** From Ref. 2.

DISCUSSION OF RESULTS

An analysis of the data obtained in terms of inductive and steric effects cannot be performed unambiguously although one trend is obvious: an increase in the steric requirements of the ketone leads to a decrease in the heat evolved when the adduct is formed. On the other hand, the inductive effect of the alkyl groups cannot be clearly seen in the heat of formation data. In principle, an increasing electron repulsion of the alkyl group ($+I$ effect)[4] should lead to an increased electron density about the oxygen atom in the ketone and thus to an increase in the $-\Delta H$-value in reactions with electron acceptors. One would therefore expect the adduct reactions to become more exothermal within the series of donors acetone, ethyl methyl ketone, isopropyl methyl ketone, and tert-butyl methyl ketone. The influence of the variation of the alkyl group in ketones upon the electron availability about the oxygen atom is clearly revealed by ionization potential measurements (Table 4).[5,6] From the data one can see that the ionization potential decreases in the radical series methyl, ethyl, isopropyl, and tert-butyl which is according to expectations. Also, the substitution of a methyl group for an α-hydrogen atom, independent of the total number of α-methyl groups, leads to an average

Table 4. First ionization potentials of ketones.[5,6]

Compound	Ionization potential, eV	Number of α-methyl groups	Difference eV
Dimethyl ketone [5]	9.71 ± 0.03	0	
Ethyl methyl ketone [5]	9.54 ± 0.03	1	0.17
Diethyl ketone [6]	9.34 ± 0.02	2	0.20
Pinacolin [5]	9.18 ± 0.03	3	0.16
tert-Butyl ethyl ketone [6]	8.98 ± 0.02	4	0.20
tert-Butyl isopropyl ketone [6]	8.82 ± 0.02	5	0.16
Di-tert-butyl ketone [5]	8.65 ± 0.03	6	0.17

decrease of the ionization potential of approximately 0.18 eV. In the enthalpy values (Table 3) an increase is found only when going from acetone to ethyl methyl ketone; a further substitution leads to a *decrease* in the $-\Delta H$-values. The change along the series is surprisingly small and whichever effect is operating it approximately counterbalances the effect from the increased electron availability at the oxygen atom. Considering the complexity of the initial and final states of the adduct formation reaction, the nature of this effect cannot even be suggested before structure data have been made available. However, an explanation can be given for the approximate constancy of the $-\Delta H$-values in the given series, although the steric requirements change quite considerably. In the adduct, the antimony atom is bound to one of the oxygen lone electron pairs and it very likely lies in or close to the plane containing the C—CO—C moiety. This means that the acceptor molecule has one of the alkyl groups as its nearest neighbour and in principle it could

occupy two different sites. In the methyl alkyl ketones discussed, the site close to the methyl group has nearly unchanged steric conditions while the opposite site gets more crowded as the alkyl group changes from methyl to *tert*-butyl. It is therefore not surprising that the $-\Delta H$-values remain relatively constant within the series and it might be concluded, that the acceptor molecule occupies the position close to the methyl group.

It is now interesting to compare the $-\Delta H$-values for isopropyl methyl ketone and diethyl ketone. The ionization potentials of the two ketones should be (almost) identical. Model studies suggest that both adducts can be formed without the introduction of any serious non-bonding interaction (strain). However, in the case of the diethyl ketone $SbCl_5$ adduct (identical sites) the ethyl group close to the acceptor has lost its rotational freedom around the carbonyl-α-carbon bond so that it is more or less "locked" in a narrow range of positions. This is probably the reason why the $-\Delta H$-value of the diethyl-ketone adduct is significantly less than that of the isopropyl methyl ketone. The effect becomes more pronounced when comparing the values for the *tert*-butyl methyl and *tert*-butyl ethyl ketones, $-\Delta H$ being 16.95 and 14.58 kcal.mole^{-1}, respectively. Also in these cases, it will seem that models of the adducts, free of strain, can be constructed (although we don't know if they represent the true picture as far as some critical bond angles and distances are concerned). However, the interlocking of the alkyl groups in the *tert*-butyl ethyl ketone adduct is much stronger than it is in the free ketone. This leads to an increased storage of vibrational energy in the adduct compared to that in the reactants, and as a result, the adduct formation becomes less exothermal. It could be, that also a direct non-bonding repulsion interaction starts to become significant in the *tert*-butyl ethyl ketone adduct which would explain the considerable decrease in the $-\Delta H$-value. The internal strain built up in the adduct becomes more pronounced when the bulkiness of the donor molecules increases in the series *tert*-butyl isopropyl ketone, di-*tert*-butyl ketone.

As a conclusion, it seems that at least three different effects must be considered in order to account for the results obtained. However, it is obvious, that a detailed analysis can be successfully made only when structural and infrared data are available.

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