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AMINE OXIDES—XIII[1]

IODINE COMPLEXES WITH NON-AROMATIC AMINE OXIDES

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Abstract—EDA–iodine complex with trialkylamine oxides in dichloromethane have been investigated spectrophotometrically. Thermodynamic (K_c^{AD}, $-\Delta G°$) and spectral (ε_λ^{AD}) characteristics of these complexes were determined. The absorption band of iodine in the visible region was blue-shifted with a variable maximum, depending on the structure of the amine oxide. The K_c^{AD} and ε_λ^{AD} values were calculated using a modified method. A non-linear relationship $K_c^{AD} = f(R)$, where R is the number of carbon atoms in the alkyl chain, was found.

Non-aromatic amine oxides are widely known and used compounds; their physico-chemical characteristics and their biological effects have been reviewed.[2] As the molecule contains a strongly polarized N—O linkage, the O atom in these amine oxides is more negative than in other O-containing compounds (alcohols, ethers, carbonyl compounds, etc.) and so it becomes a strong electron donor in EDA complexes. It is surprising that relatively little attention has been paid to complexes of amine oxides with iodine.[3–5] Kubota[3] found that the complexes of aliphatic amine oxides with iodine were substantially stronger than aromatic ones; that follows from the fact that the aliphatic amine oxides do not exist in various resonance states. Actually, the aliphatic amine oxides are very strong electron donors for BF_3, SO_2, SiF_4, SO_3, H_2O_2, etc. and the complexing ability of, e.g. trimethylamine oxides is also very important in the energy balance of biological processes.[6–8]

In this paper, we have investigated the interaction of iodine with a series of trialkylamine oxides, mainly from the view of their structure (alkyl chain length variation) affecting the electron donating ability of oxygen in the N—O linkage.

RESULTS AND DISCUSSION

Calculation of the stability constants K_c^{AD} (dm^3 mol^{-1}) and molar absorption coefficients ε_λ^{AD} (dm^3 mol^{-1} cm^{-1}) was carried out using

$$\frac{[A_0][D_0]}{A} = \left([A_0]+[D_0]-\frac{A}{\varepsilon_\lambda^{AD}}\right)\frac{1}{\varepsilon_\lambda^{AD}}+\frac{1}{\varepsilon_\lambda^{AD}K_c^{AD}} \quad (1)$$

where $[A_0]$ is the initial concentration of the acceptor (iodine) in mol dm^{-3}; $[D_0]$ the initial concentration of the donor (amine oxide) in mol dm^{-3}; and A is the shifted iodine band absorbance, used for the system of comparable donor and acceptor concentrations by, e.g. Lang[9] and Kubota.[3] This equation is applicable because in the interaction of iodine with amine oxides in all cases 1 : 1 complexes were formed; this was proved also by the presence of one isosbestic point (Fig. 1). The slope of the line indicates the value $1/\varepsilon_\lambda^{AD}$ and the intersection on the y-coordinate axis is $1/\varepsilon_\lambda^{AD}K_c^{AD}$.

Equation (1) should be solved by iteration, where so called apparent ε and K_c values were chosen or calculated; the mentioned procedure was in our case modified in such a way that we iterated two limit lines, given by chosen limit values of apparent ε; this resulted in a line satisfying Eq. (1). Calculation of the ε_λ^{AD} and K_c^{AD} values consisted of the following steps:

$$y_i = \frac{[D_0]_i[A_0]_i}{A_i}$$

$i = 1, 2, 3, \ldots, n$
n = number of applied donor concentrations

$$x_{i1} = [D_0]_i + [A_0]_i - \frac{A_i}{\varepsilon_{min}}$$

$$x_{i2} = [D_0]_i + [A_0]_i - \frac{A_i}{\varepsilon_{max}}.$$

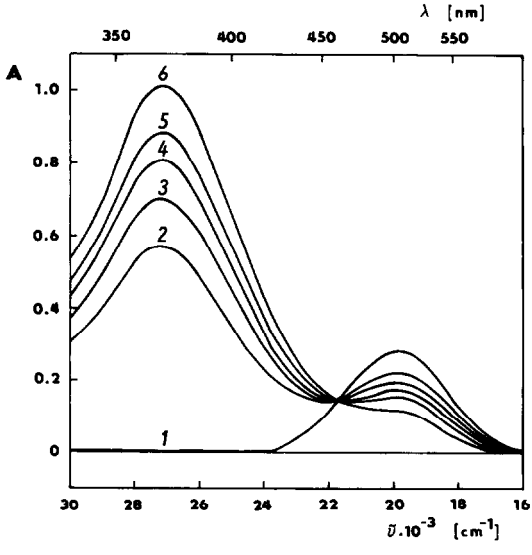

Fig. 1. Absorption spectrum of decyldimethylamine oxide complex with iodine in dichloromethane at 293.15 ± 0.1 K. Acceptor concentration: 3.1×10^{-4} mol dm^{-3}; donor concentration: 0 for line 1, 1.328×10^{-4} mol dm^{-3} for line 2, 1.634×10^{-4} mol dm^{-3} for line 3, 1.940×10^{-4} mol dm^{-3} for line 4, 2.247×10^{-4} mol dm^{-3} for line 5, 2.859×10^{-4} mol dm^{-3} for line 6.

Table 1. Amine oxides $R(CH_3)_2N\oplus—O\ominus$

No.	R	Formula M_r	M.p.[a] (°)	Yield (%)
1	methyl	C_3H_9NO 75.11	218–220[b]	55[c]
2	butyl	$C_6H_{15}NO$ 117.19	146–148[b]	72
3	hexyl	$C_8H_{19}NO$ 145.24	137–139[b]	68
4	octyl	$C_{10}H_{23}NO$ 173.30	125–128	78
5	decyl	$C_{12}H_{27}NO$ 201.35	133–136	75
6	dodecyl	$C_{14}H_{31}NO$ 229.40	130–134	81
7	tetradecyl	$C_{16}H_{35}NO$ 257.46	125–129	82
8	hexadecyl	$C_{18}H_{39}NO$ 285.51	126–130	83
9	1-methyldodecyl	$C_{15}H_{33}NO$ 243.44	95–97	86
10	tributylamine oxide	$C_{12}H_{27}NO$ 201.35	108–110	76
11	tridodecylamine oxide	$C_{36}H_{75}NO$ 538.01	50–53	85

[a] Uncorrected.
[b] Capillary tube.
[c] After three-fold sublimation.

Linearization of the line by the least squares method gives

$$y = ax + b, \quad a = \frac{1}{\varepsilon}, \quad b = \frac{1}{\varepsilon K_c}$$

$$a = \frac{\Sigma x_i y_i - \dfrac{\Sigma x_i \Sigma y_i}{n}}{\Sigma x_i^2 - \dfrac{(\Sigma x_i)^2}{n}}, \quad b = \frac{1}{n}(\Sigma y_i - a\Sigma x_i).$$

The variation of introduced ε_{min} and ε_{max} and comparison of a_1 and a_2, and b_1 and b_2, respectively, were put in the program with a maximum deviation of 0.1%. The minimum value (ε_{min}) was different for each compound, but always in the region 1.8×10^3–6.8×10^3, and was affected by two factors:

(a) by the linear course of the corresponding line;
(b) by positive values of the slope of the line and the intercept on the y-axis.

The maximum (ε_{max}) value of the apparent molar absorption coefficient was 10^6 for all compounds; the continuing increase of this value has not changed the slope of this line significantly.

The results (K_c^{AD}, ε_λ^{AD} and $-\Delta G^\circ = 2.303RT \log K_c^{AD}$) are summarized in Table 2. For K_c^{AD} in the region of complex formation Person[10] derived a relationship, according to which the found K_c^{AD} values can be regarded as true ones, if

$$\frac{0.1}{K_c^{AD}} \leqslant [D_0] \leqslant \frac{9}{K_c^{AD}}$$

where $[D_0]$ is an arbitrary donor concentration, which

Table 2. Stability constants, ε_λ^{AD} and $-\Delta G^\circ$ values of the charge-transfer complexes between trialkylamine oxides and I_2 in CH_2Cl_2 solutions at 293.15 ± 0.1 K

No.	λ (nm)	ε_λ^{AD} ($dm^3\ mol^{-1}\ cm^{-1}$)	K_c^{AD} ($dm^3\ mol^{-1}$)	$-\Delta G^\circ$ (kJ $dm^3\ mol^{-2}$)	$\Delta\lambda$[a] (nm)
1	392	4989 ± 75	1865 ± 140	18.4	115
2	392	4089 ± 307	2141 ± 295	18.7	115
3	392	3838 ± 162	3081 ± 283	19.6	115
4	385	5570 ± 229	4279 ± 616	20.4	122
5	368	9604 ± 98	5112 ± 293	20.8	139
6	368	10,959 ± 166	5635 ± 186	21.1	139
7	368	9934 ± 246	6782 ± 595	21.5	139
8	368	10,325 ± 172	7947 ± 636	21.9	139
9	370	9620 ± 800	5792 ± 504	21.1	137
10	380	7467 ± 278	3022 ± 434	19.5	127
11	367	26,550 ± 2495	1692 ± 227	18.1	140

[a] $\lambda_{I_2} - \lambda$ (λ_{I_2} = 507 nm).

was used in the stability constant calculation at constant acceptor concentration. In our case, all K_c^{AD} values satisfy this condition.

The K_c^{AD} and ε_λ^{AD} values increase with alkyl chain length variation in alkyldimethylamine oxides (Table 2). The K_c^{AD} increase is probably related to an increase in electron donor ability of individual compounds. Also connected with this is the blue shift of the iodine band ($\Delta\lambda$), which was affected by molecule structure variation. A shift from the initial value 507 nm into the region 392–367 nm was observed (Table 2). The rate of this shift is in correlation with the electron donor abilities of investigated compounds. Mulliken and Person[11] stated that this shift is in close correlation with partial electron donation into an unfilled (in fact an anti-bonding) orbital of iodine and with an increase in the excitation energy of the molecule. Non-linearity of this shift (but also of K_c^{AD}) with variation of the alkyl chain length (Table 2) is very probably due to the change of steric configuration of alkyl chains around the polar N—O group.[12] Compound **4** (octyldimethylamine oxide) represents a transient type between "weak" (**1–3**) and "strong" (**5–8**) complexes in this group of compounds.

In the case of tributylamine oxide (**10**) in comparison with butyldimethylamine oxide (**2**) an increase of K_c^{AD} and also a larger blue shift can be explained by an increase in the inductive effect of the alkyl groups and so by an increase of oxygen electron donor ability. In tridodecylamine oxide (**11**) the electron donor ability and complexing ability are significantly affected by steric hindrance.

All phenomena affecting the amine oxide–iodine complexes have a significant effect also on the $-\Delta G^\circ$ value, this being a numeral measure of the chemical affinity of the interacting components.

The branching of a long alkyl chain in the α-position (**9**) has in principle no affect on studied values.

EXPERIMENTAL

Amine oxides. Trimethylamine oxide dihydrate was prepared by oxidation of 40% aq Me_3N soln by 30% aq H_2O_2 soln. After isolation and multiple crystallizations from an EtOH–ether mixture the resultant product had m.p. 90–93°. After azeotropic drying by benzene the product was sublimed three times *in vacuo* and anhyd trimethylamine oxide was obtained, m.p. 218–220° (capillary tube). Other amine oxides (Table 1) were prepared by oxidation of methanolic solns of trialkylamines by 30% aq H_2O_2 soln. After oxidation and isolation the products were thoroughly dried by azeotropic distillation with benzene and toluene, followed by multiple crystallizations (4–5 times) from dry Me_2CO and dried over P_4O_{10} in a high vacuum. The purity of the products was checked by TLC[13] and by IR spectra.

Iodine. Twice sublimed iodine, AR grade was purified by subliming twice in a N_2 atmosphere and stored in a desiccator protected from light.

Dichloromethane. Merck, AR grade was dried by P_4O_{10} and purified by distillation from P_4O_{10}. The middle fraction was used for measurements.

Data treatment. All CH_2Cl_2 solns of hygroscopic amine oxide were prepared according to Kubota[3] and the spectra were measured 15 min after the preparation of mixed solns. The iodine concentration in CH_2Cl_2 was constant and experimentally determined for every donor (2×10^{-4}–4.5×10^{-4} mol dm^{-3}). The concentration of amine oxides varied from 1×10^{-4} to 5.5×10^{-4} mol dm^{-3}. The mutual donor–acceptor ratio corresponded to the region of complex forming 1:1. For every compound three independent samples were weighed; from these a series of 8–13 concentrations were prepared by dilution; three parallel determinations were always performed. The reference sample was pure CH_2Cl_2. The absorbances were followed at three wavelengths in the 400–350 nm region. In Table 2 are presented maxima of shifted iodine bands. For the measurements 1 cm matched quartz cells equipped with stoppers in temp-regulated cell holders were used. The measurements were always performed at constant temp 293.15±0.1 K on Specord UV–VIS, C. Zeiss, Jena, apparatus. The spectrophotometer was calibrated by standard $K_2Cr_2O_7$ soln[14] and with a standard holmium filter.

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