The Electric Dipole Moment of Trialkylamine–Iodine Complexes

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THE magnitude of the electric dipole moments of trialkylamine–iodine complexes has been a matter of dispute. There is agreement that the total polarisation of such complexes in dioxan solution, at room temperature, corresponds to a very large moment of *ca.* 10—12 D (see Table 1); but Toyoda and Person[1] point out that the u.v. spectra of the solutions indicate that the iodine is present predominantly as the I_3^- ion, and they suggest therefore that the observed polarisation is largely that of ion pairs. Kobinata and Nagakura[2] have obtained what appear to be genuine dipole moments of 6—7 D for the iodine complexes of ammonia, and of primary and secondary alkylamines, in benzene and in dioxan solution (see Table 1). They made all measurements immediately after mixing and found that there is no spectral evidence of the presence of any iodine-containing anion under these conditions.

We have found that it is possible to prevent detectable decomposition of the trialkylamine–iodine complexes, even at the higher concentrations

TABLE 1

Complex	μ(D)	Solvent	T(°C)	Reference
Me_3N,I_2	6·5	Toluene	−50	This work
Et_3N,I_2	6·9	Toluene	−40	This work
Me_3N,I_2	10·05 ±0·1	Dioxan	25	1
Et_3N,I_2	12·44 ±0·1	Dioxan	25	1
Et_3N,I_2	11·3	Dioxan	20	3
Et_3N,I_2	10·5	CCl_4	25	4
Et_3N,I_2	8·9	Toluene	23	This work
Pr^iNH_2,I_2	6·2	Benzene	20	2
Pr^iNH_2,I_2	7·2	Dioxan	20	2
$EtNH_2,I_2$	6·2—6·6	Benzene	20	2
Et_2NH,I_2	6·2	Benzene	20	2
Et_2NH,I_2	7·0	Dioxan	20	2
NH_3,I_2	6·1—6·7	Dioxan	20	2
Py,I_2	4·90±0·3	Dioxan	25	1
Py,I_2	4·5	Cyclohexane	25	5
Py,I_2	6·24	CCl_4	25	6
Py,I_2	5·7	CCl_4	25	4

necessary for dielectric measurements, by mixing the components, and making measurements on solutions, at −40° or −50°.

Tsubomura and Nagakura[3] found that solutions of the triethylamine–iodine components in n-heptane in high enough concentration for useful electric polarisation measurements were 'unstable' at room temperatures. We were unable to use this solvent at −40° because the complex was far too insoluble, nor of course could we use benzene or dioxan. We therefore used toluene.

The values of the dipole moment obtained for the tertiary amine complexes are very similar to those reported by Kobinata and Nagakura for those of non-tertiary amines and are considerably lower, therefore, than all values reported previously, but they are larger than most of the values reported for the pyridine–iodine complex (see Table 1).

It seems unlikely that the complexes dissociate into ions at the low temperatures we used both because of the size of the dipole moments obtained and because the dielectric constants of these solutions did not change with time. Similar solutions made up at room temperature showed a change of dielectric constant and gave a large moment (see Table 1). However, we wished to satisfy ourselves completely, if possible, that no ion pairs were present.

When an examination was made of the u.v.–visible spectrum of a solution of the complex in toluene at room temperature (with a solution containing the same concentration of amine, but no iodine, as reference) absorption peaks could be observed at 294 and 363 mμ, with molar extinction coefficients 17,800 and 6,900 respectively. These peaks are characteristic of the spectrum of I_3^-.[7] They were observed in solutions of the same concentration as those used for dielectric measurements, with a 0·06 mm. cell. They were also to be seen in more dilute solutions using a 1 cm. cell. The intensity of absorption at these peaks increases for a time immediately after making up the solutions, approximately doubling over as long as 6 hr. in the most dilute solutions, but we did not find any decreasing peak.

Cold solutions were made up in exactly the same manner as those used for dielectric measurements, but more dilute, being of a suitable concentration for observation in an 8 mm. low-temperature spectrophotometric cell.[8] When examined at −40° these showed only one absorption peak, at 393 mμ and extinction coefficient 3200—3600 depending on concentration. This peak we attribute to the shifted visible absorption band of I_2 (*cf.* Kobinata and Nagakura, Table 2). The charge transfer peak cannot be observed in toluene solution.

We have no thin cell suitable for low-temperature spectroscopy, and in the 8 mm. cell solutions of the same concentrations as we used for dielectric measurement were almost totally black for wavelengths shorter than 430 mμ. There was however barely detectable light transmission between *ca.* 345 and *ca.* 377 mμ followed by complete absorption between 380 and 395 mμ, and then transmission was again perceptible. This does argue against a peak at 363 mμ and therefore against the presence of I_3^-, even if it is not certain evidence for the presence of one at 393 mμ. In neither this nor the more dilute solution did the intensity of absorption vary with time.

TABLE 2

Donor	Solvent	T(°c)	λ_{vis}(mμ)	Molar extinction coefficient, ($10^{-3}\epsilon$)	Reference
Pr^iNH_2	Dioxan	22·5	372—375	2·0—2·9	3
	Benzene	22·5	380	2·7	3
	n-Heptane	22·5	412	1·5	3
Et_2NH	Dioxan	22·5	385	2·2	3
	n-Heptane	22·5	410	—	3
Et_3N	Toluene	−40	393	3·2—3·8	This work
	Toluene	20	363	6·1—6·9	This work
			294	17·8	
Et_3N	Dioxan	20	363	5·7	1
			295	9·8	

We conclude, therefore that the values we report represent the dipole moments of the trialkylamine complexes.

The scalar excess moments, *i.e.* $\mu_{complex} - \Sigma\mu_{components}$ for the complexes with primary, secondary, and tertiary amines are sufficiently variable to make precarious any generalisation about the connexions between them and measures of basic character such as the formation constants. They are more remarkable for their similarity than for their difference.

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