in Fig. 2 are very likely affected by such double-layer binding. Since with the smaller hydrated cations a greater number of cations can be accommodated in the ionic atmosphere, the enhanced electrostatic shielding effect would be expected to contribute to the contraction of the polymer coil. It is noteworthy that, if the intrinsic viscosity is plotted against the β_{MD}-values obtained from dialysis measurements, the curves for K^+ and Cs^+ lie quite close to the curve for Li^+. Unfortunately, since we do not know how to separate the effects of double-layer binding and of ion-bridging on $[\eta]$, these results do not supply any additional information concerning the ion-bridging of K^+ and Cs^+, which was postulated previously on the basis of other evidence.[5]

Molecular Dimensions and Binding Constants.—The previously mentioned explanation of the observed increase in the binding constant between a cation and a PO_3^--group with increasing (M^+) in terms of a contraction of the polymer coil[5] is tested in Fig. 3 where K_{TMA}[5] is presented as a function of $[\eta]$. It is seen that, to a first approximation, K_{TMA} is a function of $[\eta]$ alone, regardless of which alkali metal ion is employed. This result is consistent with and strongly supports the preceding explanation.

NEW BRUNSWICK, N. J.

[CONTRIBUTION FROM THE LABORATORY OF MOLECULAR STRUCTURE AND SPECTRA, DEPARTMENT OF PHYSICS, THE UNIVERSITY OF CHICAGO]

Molecular Complexes and their Spectra. XI. The Interaction of Iodide with Tri-*n*-Butyl Phosphate[1]

BY HIROSHI TSUBOMURA[2] AND JONATHAN M. KLIEGMAN

RECEIVED SEPTEMBER 18, 1959

The interaction between iodine and tri-*n*-butyl phosphate (tBP) has been studied spectroscopically. The visible iodine band in *n*-heptane solution shifts from 525 to 450 mμ as a result of the complexing with tBP. From quantitative measurements of the intensity of the shifted iodine band at various concentrations and temperatures, it has been found that iodine and tBP form stable 1:1 complex, with ΔH of −2.94 kcal./mole and ΔS of −3.99 e.u. The ΔH value obtained is intermediate between those for the iodine complexes with ether and ethanol. Using perfluorohydrocarbon as a solvent, an absorption tail has been found for the complex at about 220 mμ, which is considered to be a part of the charge-transfer band of this complex with its peak lying at a shorter wave length. Taking into account the electronic structure of tBP, it is concluded that iodine interacts mainly with the oxygen atom which is directly bonded with the phosphorus atom. It has also been found that tBP does not interact specifically with π-acceptors such as *p*-quinone and tri-nitrobenzene.

Introduction

It has been found that tri-*n*-butyl phosphate (tBP) can extract nitric or hydrochloric acid from their aqueous solutions. Tuck[3] suggested the formation of a complex such as $(RO)_3P{=}O{-}HNO_3$. These results seem to indicate that tBP may have a fairly strong affinity toward such Lewis acids as iodine. In this paper, the interaction between iodine and tBP is studied by the spectrophotometric method.

Experimental

The purification of iodine and *n*-heptane was described elsewhere.[4] The tBP used was a Fisher Purified Reagent; its refractive index was found to be n^{20}_D 1.42486, very close to the literature value (1.42496). However, the *n*-heptane solution of this substance and iodine showed two time-dependent absorption bands in the near ultraviolet region, which later were found to be caused by a small amount of impurities. Distillation of tBP at 9 mm. leads to a slight decomposition, but distillation at 1 mm. was carried out without decomposition (b.p., 99°). The *n*-heptane solution of this distilled substance and iodine showed absorption spectra in the visible and ultraviolet region which did not change with time for at least one day. The *p*-quinone and the tri-nitrobenzene were Eastman Pure Organic Chemicals, the former being further purified by sublimation. The tri-*n*-butyl phosphite used was the "Practical" grade of the Eastman Organic Chemicals, further purified by distillation at 5 mm. with a b.p. of 104°. The perfluorohydrocarbon was given to our Laboratory several years ago by the Minnesota Mining and Manufacturing Co. It has a boiling region from 80° to 104°. Its infrared spectrum is similar to that of perfluoroheptane. Therefore, this material is considered to be a mixture of perfluorohydrocarbons, with the number of carbon atoms lying between 7 and 8. This material has ultraviolet absorption beginning at 300 mμ but can be purified by passing it through a column of silica gel, until no absorption band is found in the region above 220 mμ.

The visible and ultraviolet absorption spectra were measured with a Spectracord. A thermostated cell holder described in the previous paper[4] was used to maintain the temperature of the cell constant.

Results and Discussion

Visible Absorption Spectra.—The visible absorption spectra of the *n*-heptane solutions of iodine and tBP are shown in Fig. 1; tBP has no absorption in this range. It can be seen that a complex is formed between iodine and tBP, a new absorption band appearing with a peak at 460 mμ, which is most reasonably assigned to the visible iodine band shifted by complex formation. The corresponding free iodine band has its peak at 525 mμ.

Assuming a 1:1 association equilibrium, the equilibrium constant has been calculated from the intensities of the spectra of various solutions at 450 mμ. The wave length 450 mμ was chosen because the ratio of the intensity of the complexed to the free iodine band is the largest at that wave length. The determination of the equilibrium constant in this case is complicated owing to the superposition of the free iodine band with that of the complexed iodine. The method adopted

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[1] This work was assisted by a grant from the National Science Foundation.

[2] On leave of absence from the Institute for Solid State Physics, The University of Tokyo, Tokyo, Japan.

[3] D. G. Tuck, *J. Chem. Soc.*, 2783 (1958).

[4] H. Tsubomura, THIS JOURNAL, **82**, 40 (1960).

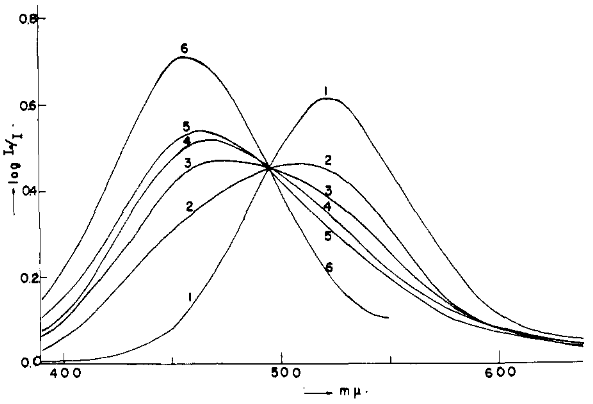

Fig. 1.—Visible absorption spectra of the n-heptane solutions of iodine (0.6744 × 10^{-3} M) and tri-n-butyl phosphate at 25° for 1 cm. cell. The concentrations of tri-n-butyl phosphate are: (1) zero, (2) 0.03031 M, (3) 0.06062 M, (4) 0.09093 M, (5) 0.12124 M, (6) calculated curve for complete complexing.

here is to assume an approximate K value, and calculating the concentration of free iodine in each solution with this K value, then the absorbance of free iodine in the solutions is calculated and subtracted from the observed absorbances to obtain the absorbance of the complex. Modified Benesi–Hildebrand plots[4] are made for these absorbance values. The K values obtained from the plots are again used for the calculation of the free iodine absorption intensity. This process is repeated until the two successive K values agree within the experimental error. The measurements of the absorption intensity have been made at 10, 17, 25 and 35°. At all temperatures, the qualitative features of the spectra are the same and isosbestic points have been obtained at 492 mμ. In all cases straight lines have been obtained for the modified Benesi–Hildebrand plot. The equilibrium constants and extinction coefficients obtained at different temperatures are given in Table I. The plots of ln K *versus* $1/T$ also have given a fairly good straight line as shown in Fig. 2. The heat of formation and the change of entropy for the complex formation obtained from these are

$$\Delta H = -2.94 \text{ kcal./mole} \quad \Delta S = -3.99 \text{ e.u.}$$

TABLE I

EQUILIBRIUM CONSTANTS K AND MOLAR EXTINCTION COEFFICIENTS ϵ FOR THE I_2-tBP COMPLEX

T, °C.	K (l./mole)	ϵ (l./mole cm.)
35	16.7	984
25	19.5	1042
17	22.0	1079
10	25.0	1064

Near Ultraviolet Spectra.—From the results obtained, it can be seen that both the heat of formation and the shift of the visible band in the I_2–tBP complex are intermediate between those for the iodine complexes with ether and alcohols.[5] If the complex between tBP and iodine is a charge-transfer complex, there must be a charge-transfer absorption band, and in view of the fairly strong interaction between tBP and iodine as can be seen from the shift of the visible band of iodine and the ΔH value above mentioned, it seems reasonable to assume that the charge transfer band will appear in the near ultraviolet region.

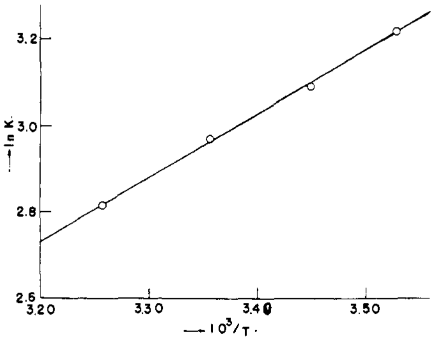

Fig. 2.—Plots of ln K *versus* $1/T$ for I_2-tri-n-butyl phosphate complex.

In Fig. 3, the spectra of the n-heptane solutions of iodine and tBP in the near ultraviolet region are given. Pure tBP liquid has a small absorption below 260 mμ, as shown in the figure, and the 0.1 M heptane solution shows no absorption except a very slight one near 220 mμ. The strong absorption shown by the n-heptane solutions of iodine and tBP which has its beginning at 250 mμ can be assigned to the I_2–heptane contact charge transfer absorption.[6] It can be seen that the contact charge-transfer band diminishes in intensity as the concentration of tBP increases and a slight absorption band arises at about 280 mμ. This latter band is situated at nearly the same wave length as those of the I_4 species[7] and may perhaps be assigned to a complex such as tBP—I_2-I_2—tBP. However, it seems more likely that it is due to an impurity still remaining in the distilled tBP, since

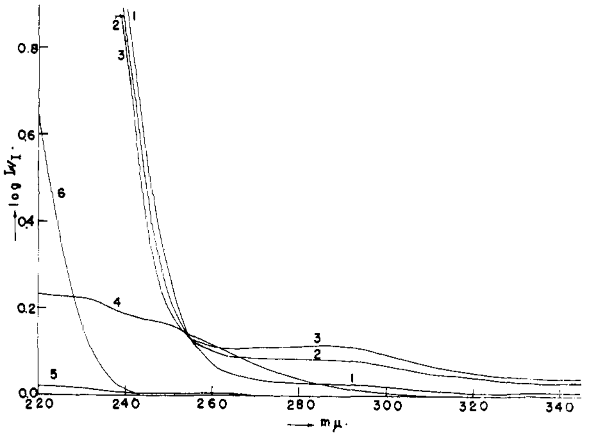

Fig. 3.—Ultraviolet absorption spectra of the n-heptane solutions of iodine and tri-n-butyl phosphate at about 25° for 1 cm. cell: (1) I_2, 0.674 × 10^{-3} M, tBP, zero; (2) I_2, 0.674 × 10^{-3} M, tBP, 0.0312 M; (3) I_2, 0.674 × 10^{-3} M, tBP, 0.0936 M; (4) tBP pure liquid; (5) 0.1 M n-heptane solution of tBP; (6) saturated solution of I_2 and tBP in perfluorohydrocarbon.

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(5) P. A. D. de Maine, *J. Chem. Phys.*, **26**, 1192 (1957).

(6) D. F. Evans, *ibid.*, **23**, 1424 (1955); *J. Chem. Soc.*, 4229 (1957); L. E. Orgel and R. S. Mulliken, THIS JOURNAL, **79**, 4839 (1957).

(7) P. A. D. de Maine, *J. Chem. Phys.*, **24**, 1091 (1956).

the peak position nearly coincides with the absorption band which appeared strongly in the solution of iodine and raw tBP. (See the Experimental part.) The diminishing of the intensity of the contact absorption can be very reasonably explained by the complexing of the iodine molecule with tBP, which inhibits the contact of iodine with *n*-heptane. From the foregoing results, it is clear that the I_2–tBP complex has no charge-transfer band above 250 mμ.

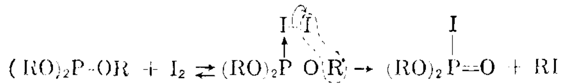
An attempt then was made to find a charge-transfer band in the region below 250 mμ. The first attempt, by using a solution of iodine in distilled tBP, was unsuccessful, since the solution showed two strong peaks at 295 and 366 mμ, which seemed to be caused by either impurities or reaction products. Therefore, a solution of iodine and tBP in perfluorohydrocarbon was prepared. As the solubility of iodine and tBP in this solvent is very low, the solutions saturated with both the two compounds were prepared, the upper tBP layer was removed and the spectrum of the perfluorohydrocarbon layer was measured. It was found that, although the saturated solutions of either tBP or iodine in this perfluorohydrocarbon had no absorption throughout the whole ultraviolet region above 220 mμ, the solution where both iodine and tBP were saturated showed absorption as shown by curve 6 of Fig. 3. The concentration of iodine in its saturated perfluorohydrocarbon solution may be considered to be about 0.0005 *M*, in view of the intensity of the visible iodine band, if the peak molar extinction coefficient of the iodine band in this solution is assumed to be nearly the same as that in *n*-heptane. The concentration of iodine in the perfluorohydrocarbon where tBP and iodine are saturated must be a little larger than that of the saturated perfluorohydrocarbon solution of iodine. The color of the solution is yellowish compared to the violet iodine solution of this perfluorohydrocarbon, suggesting that the concentration of tBP is high enough that most of the iodine molecules present in the solution are complexed with tBP.

The absorption which appeared in the ternary solution near 220 mμ may be considered as the tail of the charge transfer band between iodine and tBP. According to de Maine, the maxima of the charged transfer bands of the iodine complexes with aliphatic alcohols and ether appear between 240 and 250 mμ. The charge-transfer band of the I_2–tBP complex is, therefore, at much shorter wave length.

Not much is known about the electronic structure of the alkyl phosphates. Gillis, Horwood and White[8] concluded from the measurements of the molar refraction of tri-alkyl phosphates that the structure of these compounds can be described more suitably by $(RO)_3P^+ \rightarrow O^-$ than by $(RO)_3P{=}O$. But chemical evidence seems to suggest that the bond is more $P{=}O$ than $P^+ \rightarrow O^-$.[9] This bond is no doubt more or less intermediate between these two structures. It is then a question whether the RO group or the P=O group behaves more as an electron donor in the complex with iodine. From the electron withdrawing nature of the P=O group, we may assume that the oxygen atom in the P=O group is somewhat negatively charged while those in the RO groups are less negatively charged, and hence the oxygen atom in the former group may act more as a donor than the latter. It would be interesting to study the interaction of iodine with trialkyl phosphine oxide, in order to see whether the P=O group alone has a strong complexing ability with iodine.

Interaction between tBP and π-Acceptors.—In order to see whether there is any specific interaction between tBP and organic π-acceptors, dilute *n*-heptane solutions of *p*-quinone and trinitrobenzene were prepared and 1 volume of each of these solutions was mixed with 2 volumes of tBP. It was found that the near ultraviolet spectra of quinone and trinitrobenzene were shifted toward longer wave lengths by addition of tBP. The amount of shift was of the same order as that by mixing the same amount of ethanol (10–20 mμ). We cannot conclude definitely whether this shift is due to complex formation or to ordinary solvent effects. However, it seems unlikely that tBP and the π-acceptors form complexes, since there has been no indication that ethyl alcohol makes any specific interaction with such acceptors. Sterically the situation is unfavorable for complex formation in both cases. *n*-Donors such as alcohols and alkyl phosphates cannot interact with the lowest vacant molecular orbitals (m.o.) of the π-acceptors, because these m.o.'s are usually antisymmetric with respect to the plane of symmetry perpendicular to the benzene ring, while the donor orbitals are symmetric when they are directed toward the center of the benzene ring of the π-acceptors. Hence, the *n*-donors must interact with particular groups of the π-acceptors (local interaction). As triethylamine, a strong *n*-donor, has been found to give an intense red color with either *p*-quinone or trinitrobenzene, there must be a local interaction between these compounds. It may be considered that a certain energy of activation is necessary for a local interaction to occur, and alcohols and alkyl phosphates may not be sufficiently strong *n*-donors to overcome that energy of activation.

Interaction between Iodine and Tri-*n*-butyl Phosphite.—When a drop of tri-*n*-butyl phosphite is added to a dilute *n*-heptane solution of iodine, it was found that a yellow turbid solution, which is apparently due to formation of very fine crystals, was formed immediately, and almost instantaneously this solution became colorless. When the solution was precooled by a Dry Ice–acetone mixture, the yellow turbid state of the solution was fairly stable and lasted for over ten minutes. It seems very likely that the phosphite first forms a strong charge transfer complex with iodine and then a further reaction occurs, leading to the formation of dialkyl phosphoiodate and alkyl iodide.



$$(RO)_2P{-}OR + I_2 \rightleftarrows (RO)_2\overset{\overset{\displaystyle I{-}I}{\uparrow}}{P}\,O\,R \rightarrow (RO)_2\overset{\overset{\displaystyle I}{|}}{P}{=}O + RI$$

A similar reaction between bromine and tri-alkyl

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[8] R. G. Gillis, J. R. Horwood, G. L. White, THIS JOURNAL, **80**, 2999 (1958).

[9] Suggestion by Professor E. V. Jensen.

phosphite has been reported by Gerrard and Jeacocke[10] leading to the formation of dialkyl phosphobromidate and alkyl bromide. They also proposed that the reaction is initiated by the cationic attack of bromine, followed by the cleavage of the R–O bond by the nucleophilic attack of the bromine negative ion. Their explanation seems very close to the present one.

The yellow intermediate formed in the present experiment is so turbid that no absorption spectral measurements can be made. However, the yellow color seems to indicate the formation of a strong charge-transfer complex between phosphite and iodine, because most of the solutions of iodine complexes have colors which are intermediate between red and yellow, and the strongest complex of iodine so far found, the I_2-triethylamine complex, is yellow.[11] Therefore this reaction may be considered as evidence for the presence of a charge-transfer complex as the reaction intermediate.[12]

The second step of the reaction is considered to be performed by the attack of the iodine negative ion from the back side of the carbon atom of the *n*-butyl group ($\mathrm{SN_1}$ mechanism). This has been confirmed by Gerrard and Jeacocke who showed that tris {(+)-1-methylheptyl} phosphite and bromine produced (−)-1-methylheptyl bromide.

One can expect that the second step will be retarded in the case of the reaction between iodine and tri-*t*-butyl phosphite, because the attack of iodine negative ion will be much more difficult in that case due to the large *t*-butyl group. One might then reasonably hope to find an absorption band due to a charge transfer complex between iodine and tri-*t*-butyl phosphite.[13] The synthesis of tri-*t*-butyl phosphite was tried in our Laboratory by the method of Kosolapoff.[14] Unfortunately we did not succeed in that synthesis and at present no further research in this line is contemplated.

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(10) W. Gerrard and G. J. Jeacocke, *J. Chem. Soc.*, 3648 (1954).

(11) S. Nagakura, THIS JOURNAL, **80**, 520 (1958).

(12) R. S. Mulliken, *J. Phys. Chem.*, **56**, 801 (1952).

(13) This was suggested by Dr. Stanton Ehrenson.

(14) G. M. Kosolapoff, THIS JOURNAL, **74**, 4953 (1952).

CHICAGO 37, ILLINOIS

[CONTRIBUTION FROM DEPARTMENT OF CHEMISTRY, FACULTY OF SCIENCE, KYUSHU UNIVERSITY]

Effect of Solvent on *n*–π* Absorption Spectra of Ketones

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The *n*–π* absorption bands of acetone, mesityl oxide, acetophenone and benzophenone were measured in various solvents and the frequency shifts induced by solvents were analyzed on the basis of the current theory of solvent effects on absorption spectra. The results show that the well-known blue shift phenomenon in the *n*–π* absorption bands can be interpreted as the result of coöperating effects of both electrostatic and hydrogen bonding interactions on solute molecules.

Introduction

It is well known that molecules having C=O groups such as ketones usually exhibit weak *n*–π* absorption bands in the near ultraviolet region. *n*–π* absorption bands may be distinguished easily from π–π* absorption bands by a large blue shift on changing the solvent from one of lower to another of higher dielectric constant. The origin of the *n*–π* blue shift was first explained by McConnell[1] on the basis of the general solvation hypothesis. On the other hand, Brealey and Kasha[2] attributed the phenomenon of the *n*–π* blue shift essentially to the hydrogen bond formation between the solute and solvent molecules. They studied the effect of ethanol on the *n*–π* absorptions of pyridazine and benzophenone and concluded that the observed frequency shifts caused by the change of solvent from hydrocarbon to ethanol represent approximately the hydrogen bond energies in the electronic ground states. This interpretation has been criticized by Pimentel[3] on the basis of the Frank–Condon principle.

It seems certain that hydrogen bonding plays an important role in the *n*–π* blue shift phenomenon, but effects contributed by other origins are equally important and cannot be neglected. In fact, a blue shift frequently is observed even in cases where the system does not contain hydrogen bonds. In this paper we shall examine the role played by electrostatic interaction between the solute and solvent molecules in the *n*–π* blue shift in the spectra of several aromatic ketones by applying the general expression derived by McRae[4] for the solvent effect on the absorption frequency. The extent of the contribution of hydrogen bonding to the blue shift also will be considered.

Experimental

Measurements of ultraviolet absorption spectra were made on a Hitachi model EPS automatic recording spectrophotometer, using 1 cm. cells. Infrared spectra were measured on another Hitachi model EPI double beam infrared spectrophotometer, using 0.1 mm. rock salt cells.

Solvents were purified by the methods recommended by Weissberger and Proskauer,[5] and special care was taken

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(2) G. J. Brealey and M. Kasha, THIS JOURNAL, **77**, 4462 (1955).

(3) G. C. Pimentel, *ibid.*, **79**, 3323 (1957).

(4) E. G. McRae, *J. Phys. Chem.*, **61**, 562 (1957).

(5) A. Weissberger and E. S. Proskauer, "Organic Solvents," Interscience Publishers, Inc., New York, N. Y., 1955.