different degrees of branching. Also, studies of differences of solubility in the isomeric pentanes having different degrees of branching[26] would cast much light on the concepts discussed above.

The theoretical treatment has been verified in a case where the differences in internal pressures and in molar volumes are relatively small. It will be of interest to see how far from conditions of ideal solubility these equations hold. It seems as if this method, with its explicit elimination of objectionable assumptions about ΔC_p, should be of considerable value in the development of a consistent set of δ parameters.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF KANSAS, AND THE LOS ALAMOS SCIENTIFIC LABORATORY]

The Behavior of Iodine Species in Pyridine and Quinoline

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Spectrophotometric studies have been made of the behavior in pyridine and quinoline of the iodine species elementary iodine, triiodide ion and unipositive iodine ion in the absence of light. It has been shown that iodine reacts slowly with pyridine, giving rise to triiodide ion, which is relatively stable in this medium. On the other hand, iodine reacts rapidly with quinoline, forming triiodide ion, which then reacts further, but at a slower rate. No products could be isolated from solutions of iodine in quinoline. However, unequivocal evidence is offered for substitution of iodine in the quinoline nucleus. Complexes containing unipositive iodine coördinated with quinoline undergo a series of reactions with quinoline to form products apparently of polymeric nature.

In a continuation of previous work[3] on the nature of solutions of iodine in pyridine, the absorption peak in the region of 320 mμ, reported for pyridine solutions of both iodine and compounds containing the unipositive iodine–pyridine complex, could not be reproduced. Instead, it was observed that there occurs in this region a marked increase in absorption, suggesting the existence at a still shorter wave length of a peak which cannot be located because of the strong absorption of pyridine itself. This has led us to an extension of our studies to include a spectrophotometric investigation of iodine, triiodide ion and unipositive iodine complexes both in pyridine and in the stronger base quinoline. In order to eliminate the possibility of complicating photochemical reactions, all solutions were prepared under subdued light and stored in the dark except during the brief period of spectral measurements.

Experimental

Absorption Spectra.—All absorption spectra were measured with a Beckman quartz spectrophotometer, model DU, which was calibrated against the hydrogen-alpha (656.3 mμ) line. Matched silica cells, 0.5 cm. for pyridine and 1 cm. for quinoline, were used. In each case, the pure solvent was employed as a blank. Measurements at wave lengths less than 305 mμ for pyridine and 341 mμ for quinoline could not be obtained because of the strong absorption of the solvent in this region.

Materials.—Eastman Kodak Co. white label pyridine was dried for one week and distilled over barium oxide, the fraction boiling at 103.5–105.4° (574.2 mm.) being collected. It was stored in a dark bottle with moisture and carbon dioxide carefully excluded. Eastman white label quinoline was dried over potassium hydroxide pellets for two weeks, then distilled under reduced pressure. The fraction boiling at 124° (20 mm.) was collected and stored in dark bottles. Iodine (Baker C.P. analyzed) was stored in a desiccator over magnesium perchlorate and used without further purification. Eastman white label tetra-*n*-butylammonium iodide was used without further purification. The positive iodine complex compounds were prepared by the general method previously described[4] and their purity was checked by analysis.

Tetra-*n*-butylammonium triiodide was prepared in pyridine solution by addition of pyridine to a solid mixture of iodine and a 5% molar excess of tetra-*n*-butylammonium iodide. Because of the observed rapidity of reaction between iodine and quinoline, tetra-*n*-butylammonium triiodide for use in this solvent was obtained in the solid state as follows: 95% ethanolic solutions of iodine and tetra-*n*-butylammonium iodide (in slight molar excess) were mixed and the resulting black precipitate was removed by filtration, washed with 95% ethanol and dried; m.p. 67–70°, uncor.

Attempted Isolation of Reaction Products from Solutions of Iodine in Quinoline.—All attempts to isolate the products of reaction between iodine and quinoline proved unsuccessful. When sodium thiosulfate was used to remove the unreacted iodine from solutions of iodine in the amine (approximately 20 g. of iodine in 200 ml. of quinoline), a yellow crystalline product was obtained. Although this solid originally contaminated with large amounts of free sulfur, could not be completely separated from an iodine-containing impurity, and, although analyses for the product obtained from different runs varied beyond experimental limits, nevertheless each analysis showed a 1:1 sulfur:nitrogen ratio and corresponded closely to that for the formula $C_9H_7NSO_3$.

When ether was added to solutions of iodine in quinoline that had stood in the dark for a few days, dark solids, showing qualitative tests for nitrogen and ionic iodine and forming picrate derivatives containing no iodine and having the same melting point as the picrate of quinoline, were precipitated.

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[1] Department of Chemistry, University of Kansas, Lawrence, Kansas.

[2] Taken in part from the Master's thesis of Ervin Colton, University of Kansas, June, 1952.

[3] R. A. Zingaro, C. A. VanderWerf and J. Kleinberg, THIS JOURNAL, **73**, 88 (1951).

[4] R. A. Zingaro, J. Goodrich, C. A. VanderWerf and J. Kleinberg, *ibid.*, **71**, 575 (1949).

When sulfur dioxide was used in an attempt to remove the unreacted iodine from similar solutions of the halogen in the amine, dark brown solids of polymeric nature and showing qualitative tests for nitrogen and iodine were obtained.

After the excess iodine from solutions of iodine in quinoline had been removed with sulfur dioxide, attempts to convert any iodinated derivative present to a hydroxy derivative by boiling the solution with 20% sodium hydroxide solution also led to polymeric products.

It thus appears that, although the evidence for an iodinated derivative is good, isolation of the product is complicated by the labile character of the iodinated quinoline. It might be pointed out that, except for descriptions[5,6] of their original preparation, both 2- and 4-iodoquinoline are conspicuous by their absence from the literature.

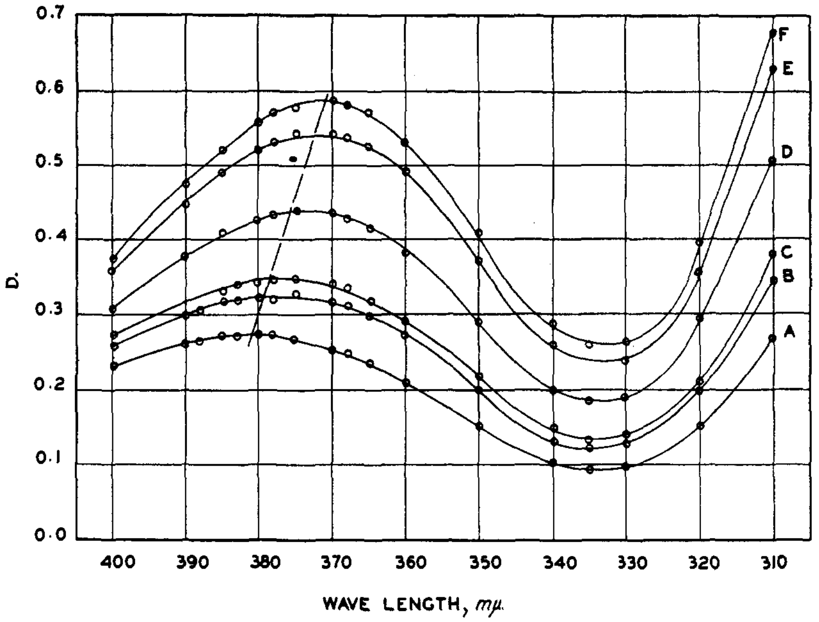

Fig. 1.—Absorption of a solution of iodine in pyridine, concn., 2 × 10^{-4} *M:* A, 0 hr.; B, 12 hr.; C, 24 hr.; D, 8 days; E, 16 days; F, 19 days.

Results and Discussion

For solutions of iodine in pyridine, there is little absorption in the region 550–400 mμ. The first strong absorption occurs at approximately 400 mμ as the beginning of a broad band with a maximum at 383–380 mμ and a peak intensity $\epsilon_{\max} \cong$ 2600–2700 (Fig. 1, curve A). This extreme shift and broadening of the absorption band characteristic of molecular iodine (maximum at approximately 520 mμ) is evidence not only of complex formation, but also for a complex of the type $\overset{+}{\mathrm{Py}}\Big\langle\begin{matrix}\mathrm{I}^-\\ \mathrm{I}\end{matrix}$, in which the valence structure of the iodine molecule has been appreciably changed.[7] Additional evidence for polarized structures of this type is the high dipole moment (μ = 4.17 × 10^{-8}) found for $C_5H_5N{\cdot}I_2$ in benzene solution.[8] The immediate and complete exchange observed between radioactive iodine and derivatives of monopyridine iodine(I) in pyridine solution[9] is also consistent with the complex structure proposed above.

As iodine–pyridine solutions are stored in the dark, two noteworthy changes in the spectra are observed: (1) a gradual rise in optical density and (2) a slow shift in the position of the absorption maximum (see broken line in Fig. 1), which reaches a value of 370 mμ after 19 days at 25°. This is indicative of a slow reaction between iodine and pyridine[10] with the simultaneous formation of a new absorbing species. In view of the fact that the curve approaches in shape that of the triiodide ion, which in pyridine was shown to have a maximum absorption at 368 mμ with $\epsilon_{\max} \cong$ 23,500, it appears almost certain that this new species is the triiodide ion. As will be shown later, this is quite conclusively the case for solutions of iodine in quinoline. The formation of triiodide ion can best be explained as resulting from substitution of iodine in the pyridine ring with liberation of hydrogen iodide. The fact that such substitution can occur in the pyridine nucleus at room temperature, under conditions such that photochemical activation is excluded, is also indicative that the iodine exists in a highly polarized form. In the case of pyridine, evidence as to whether this substitution reaction with molecular iodine proceeds by electrophilic or nucleophilic attack is lacking.

Evidence for electrophilic attack of pyridine by

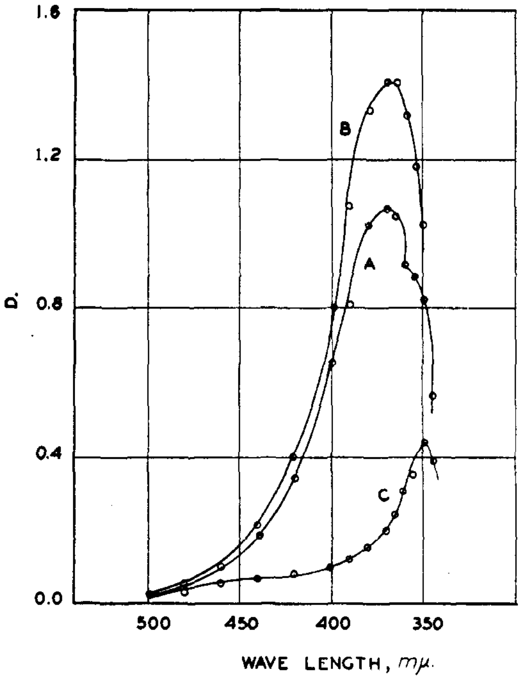

Fig. 2.—Absorption of a solution of iodine in quinoline, concn., 1.1 × 10^{-4} *M:* A, 0 hr.; B, 3 hr.; C, 2 days.

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(5) P. Friedländer and A. Weinberg, *Ber.*, **18**, 1528 (1885).

(6) A. Claus and W. Frobenius, *J. prakt. Chem.*, **56**, 181 (1897).

(7) R. S. Mulliken, This Journal, **72**, 600 (1950); **74**, 811 (1952).

(8) Ya. K. Syrkin and K. M. Anisimova, *Doklady Akad. Nauk. S.S.S.R.*, **59**, 1457 (1948).

(9) J. Kleinberg and J. Sattizahn, This Journal, **73**, 1865 (1951).

(10) Titration of iodine–pyridine solutions stored in the dark reveals a slow over-all decrease in titratable iodine. This effect is somewhat erratic, however, in that slight increases beyond the limit of experimental error are frequently observed for successive titrations, although the over-all trend is toward a decrease in iodine.

a positively charged iodine–pyridine complex is afforded by the previously reported isolation of 3-iodo- and 3,5-diiodopyridine from the reaction of various substituted silver benzoates with iodine and pyridine in chloroform,[11] and by the initial decrease in optical density with time observed for a 10^{-2} M solution of monopyridine iodine(I) *p*-chlorobenzoate in pyridine. It should be pointed out, also, that in a more concentrated (1.8×10^{-2} M) solution of monopyridine iodine(I) benzoate in pyridine the same initial decrease in optical density was noted in the region of greatest absorption, accompanied by an increase in absorption and emergence of a peak in the region of maximum absorption characteristic of solutions of iodine in pyridine.

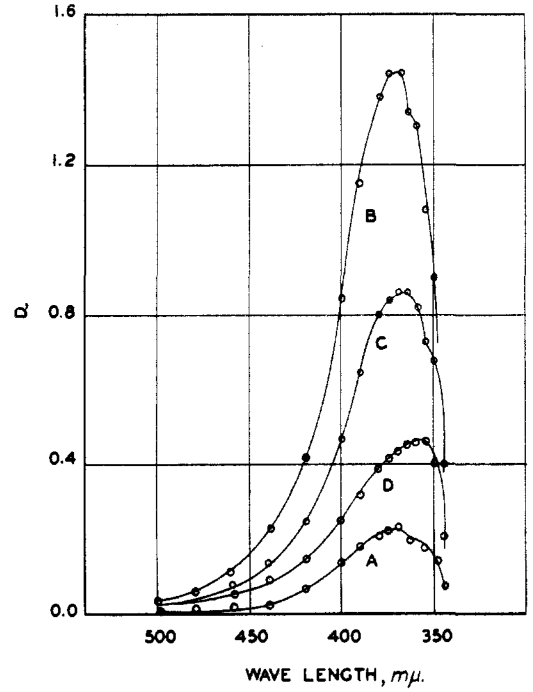

Fig. 3.—Absorption of tetra-*n*-butylammonium triiodide in quinoline: A, 2.2×10^{-5} M soln., 0 hr.; B, 1.1×10^{-4} M soln., 7 hr.; C, 1.1×10^{-4} M soln., 23 hr.; D, 1.1×10^{-4} M soln., 42 hr.

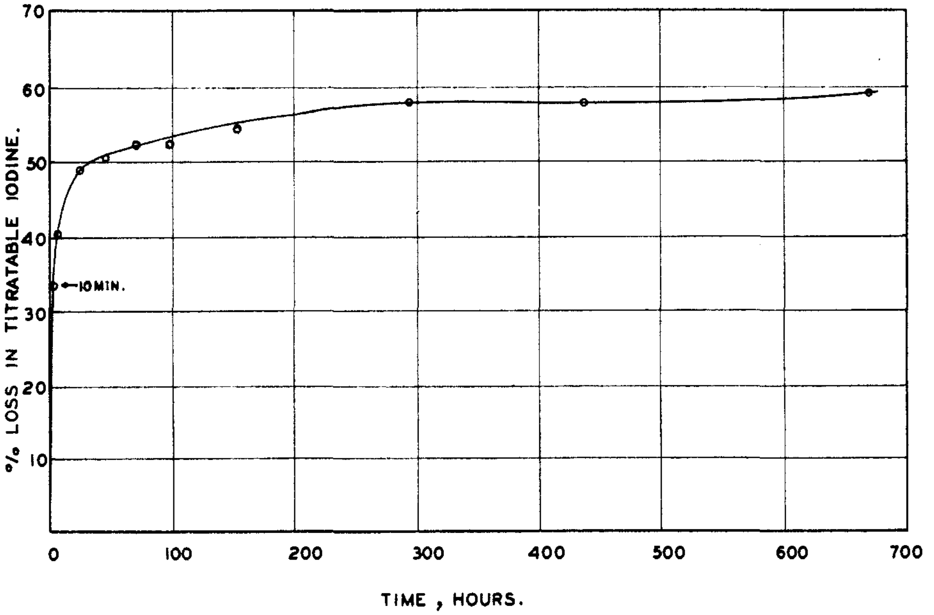

Fig. 4.—Change in titratable iodine in quinoline with time (original concentration 10^{-1} N).

In the hope that the reactions presumably occurring in pyridine solution might be speeded, and that more clear-cut evidence might be obtained as to their nature, similar studies, all conducted in the absence of light, were undertaken in the more basic solvent quinoline. As indicated by the character of the absorption curves shown in Fig. 2, a rapid reaction between iodine and quinoline does indeed occur. Immediately after mixing (curve A), an initial peak is observed at 370 mμ; a sharp increase in optical density, with *no shift* in the position of the peak, is then noted (curve B). This observation suggests that the peak is due to a species resulting from reaction between the iodine and the solvent. It seems likely, moreover, that the shoulder in curve A represents the beginning of an iodine absorption band, which, like that of iodine in pyridine, is relatively broad. Even at the outset, however, the peak of this band is masked by the presence of a more highly absorbing species, and after a short time (curve B) the shoulder is no longer noticeable. The peak at 370 mμ is attributed to triiodide ion. Evidence for this conclusion is offered by the marked similarity of these absorption curves to those of a known solution of triiodide in quinoline (curves A and B in Fig. 3), which also show a peak at 370 mμ, and, even more definitely by the rapid loss, up to 50%, of titratable iodine in solutions of iodine in quinoline (Fig. 4). The reaction of iodine is undoubtedly one of substitution, and for each mole of iodine which reacts, a second mole is required for the formation of triiodide ion with the iodide ion produced.

Upon standing the high absorption and peak attributed to triiodide ion are lost and a new peak at-

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[11] R. A. Zingaro, C. A. VanderWerf and J. Kleinberg, This Journal, **72**, 5341 (1950).

tributed to an unidentified iodinated derivative appears at 355–350 mμ (curve C, Fig. 2). Although no products could be isolated from solutions of iodine in quinoline after standing in the dark, a sulfonated derivative was obtained when the reaction mixture was treated with sodium thiosulfate (see Experimental section). It hardly seems likely that substitution of hydrogen by sulfur could have occurred without prior formation of an iodinated derivative in which iodine presumably was labile.

It is somewhat surprising that the relatively stable triiodide ion also reacts with quinoline, although at a much slower rate than free iodine itself. Evidence of such reaction is to be found first in the gradual disappearance of the triiodide peak (curves B and C, Fig. 3) in solutions of an authentic triiodide in quinoline, and also in the nature of the iodine titration curve (Fig. 4), which shows that, after 50% of the iodine has been lost and the remainder presumably exists as triiodide ion, slow loss of titratable iodine nevertheless continues. The fact that the reaction is again one of substitution is also indicated by the eventual emergence of the characteristic peak at 355 mμ, attributed to an iodinated derivative. It seems probable that the reaction proceeds *via* free iodine formation according to the equation

$$I_3^- + \text{Quin} \rightleftarrows I^- + \text{Quin}\cdot I_2$$

The relatively strong base quinoline here partially displaces the weaker base iodide ion from its complex with molecular iodine, and the equilibrium is driven toward completion through decrease of $\text{Quin}\cdot I_2$ concentration as an iodinated derivative is formed. The presence of the $\text{Quin}\cdot I_2$ complex may perhaps be responsible for the shoulders in curves A and B, Fig. 3, which occur at approximately the same wave length as that in curve A of Fig. 2, attributed to iodine in quinoline. The behavior of triiodide ion in pyridine stands in marked contrast to that in quinoline; in the former solvent triiodide ion, as shown by spectrophotometric studies, remains relatively unchanged after several weeks of standing in the dark. This difference may be due to the lesser basicity of pyridine as compared with quinoline.

Freshly prepared quinoline solutions of a series of substituted benzoates (*e.g.*, *o*-, *m*- and *p*-chlorobenzoates, *o*- and *m*-iodobenzoates and *m*- and *p*-nitrobenzoates) of monoquinoline iodine(I), all show an absorption maximum in the region 355 mμ, $\epsilon_{\max} \cong 200$, and obey Beer's law at this wave length. Rather rapid reaction involving removal of unipositive iodine, followed by formation of triiodide ion, is indicated by the initial decrease in optical density at 355 mμ (curves A and B, Fig. 5) and the subsequent gradual rise in optical density with appearance of a new peak at 370 mμ (curve C, Fig. 5). Finally this peak disappears and a third peak is observed in the region of 355 mμ (curve D). It is unlikely that this last peak is due to unipositive iodine species; it may probably be attributed to a substance which could be readily isolated from the mixture in the form of a violet, amorphous, polymeric solid, containing nitrogen and iodine, and which was found to give an absorption maximum at 355 mμ in quinoline solution. These facts suggest a complex series of reactions in which the initial product gives rise to iodine with polymerization.

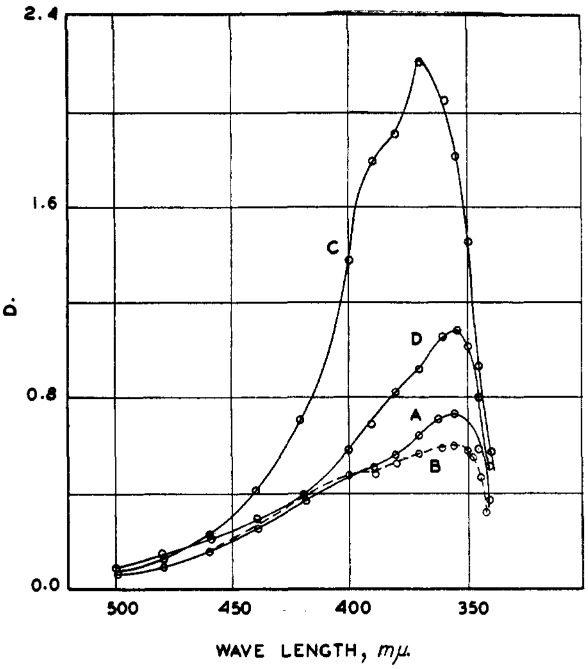

Fig. 5.—Absorption of monoquinoline iodine(I) benzoate in quinoline, concn., 0.00 *M:* A, 0 hr.; B, 4 hr.; C, 9 hr.; D, 5 days.

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