

stead, by fitting eq. 8 to the experimental values of \bar{a} and S^{19} for a single experimental point, $N_w = 0.703$. From this single data point, we obtained $K' = 0.105$. We have plotted both eq. 8 and 9 in Figure 3 with S and Q as common abscissa. All data points obtained in the water–DMSO system are thus included in Figure 3 at least once. The excellent agreement of experimental points with eq. 8 and 9 over the entire range of solvent composition lends support to the radical–solvent complexing theory of GFF, as well as to the specific solvation model employed in this work. The

symmetry of the two curves in Figure 3 is an accidental consequence of the result that $KK' \sim 1$, and is not a general consequence of the theory.

The failure of the data of the water–ACN system to agree quantitatively with the theory may reflect an oversimplification of the solvation model for this particular system, errors in the activity measurements, or both.

Acknowledgment. The authors gratefully acknowledge financial support by the National Science Foundation and the use of the facilities of the MIT Computation Center.

Molecular Complexes and Their Spectra. XVIII. Iodine Complexes with Tertiary Amine N-Oxides^{1a,b}

Tanekazu Kubota²

Contribution from the Laboratory of Molecular Structure and Spectra, Department of Physics, University of Chicago, Chicago, Illinois 60637.

Received June 26, 1964

The 1:1 iodine complexes of aromatic and aliphatic tertiary amine N-oxides were studied spectrophotometrically in carbon tetrachloride for the former and in dichloromethane for the latter. The typical compounds used are pyridine N-oxide (I) and N-methylbenzaldoxime (II) for the former, and for the latter tribenzylamine N-oxide (III) and trimethylamine N-oxide (IV). The visible iodine band shifted to 441, 446, 393–394, and 391–392 $m\mu$ on complex formation with I, II, III, and IV, respectively. The following values of K (l./mole), ΔH (kcal./mole), and ΔS (e.u.) for the complexes were determined by intensity measurement of these shifted iodine bands: 77.9 (at 23°), –5.85, and –11.0 for I; 35.8 (at 15°), –5.25, and –11.2 for II; 3470 (at 20°), –10.5, and –19.6 for III; and 5660 (22°), –10.0, and –16.9 for IV, respectively. These values are discussed and compared with the iodine complexes with other oxo compounds; it is concluded that the oxygen atom in the N→O bond is the active center for complex formation, and that the complexes with aliphatic tertiary amine N-oxides are more stable than those with the aromatic N-oxides, while the latter complexes in turn are more stable than the iodine complexes of other usual oxo compounds. Ultraviolet absorption spectra as affected by complex formation were recorded under various conditions and are discussed from the viewpoints of hydrogen bonding and salt formation effects on these N-oxides, the spectra of the donors themselves in the complexes, and the effect of complex formation in eliminating the contact charge-transfer band between iodine and dichloromethane. Various spectral constants pertinent to the shifted iodine bands, charge-transfer bands, etc., are shown in Table II.

Introduction

Since tertiary amine N-oxides contain the semipolar bond $\geq N \rightarrow O$ and show a large dipole moment,³ the oxygen atom here is doubtless more negative than in usual oxo compounds like alcohols, ethers, amides, and so on, whose iodine complexes were studied spectroscopically by many workers,⁴ and a comparative study of the characteristics of the iodine complexes with these N-oxide compounds is then of special interest. In the present paper, we report quantitative spectroscopic and thermodynamic studies of iodine complexes with pyridine N-oxide (I), N-methylbenzaldoxime (II), tribenzylamine N-oxide (III), and trimethylamine N-oxide (IV). Compounds I and II are typical conjugated amine N-oxides as shown in I_{a,b,c} and II_{a,b,c} where oxygen 2p π -electrons can conjugate with the rest of the π -electron systems.^{3,5,6} On the other hand, compounds III and IV, which are aliphatic tertiary amine N-oxides, seem to be different from those of the conjugated type, because in these molecules the N⁺–O[–] dative bond cannot conjugate with another π -electron system. The oxygen atom in the aliphatic type of amine oxides should then be more negative and a stronger donor for iodine than that in the conjugated type, an expectation which is confirmed by the much larger values of pK_a ⁷ and

(3) (a) A. N. Sharpe and S. Walker, *J. Chem. Soc.*, 4522 (1961); (b) A. R. Katritzky, E. W. Randall, and L. E. Sutton, *ibid.*, 1769 (1957); (c) E. P. Linton, *J. Am. Chem. Soc.*, **62**, 1945 (1940); (d) T. Kubota, M. Yamakawa, and Y. Mori, *Bull. Chem. Soc. Japan*, **36**, 1552 (1963).

(4) H. Tsubomura and R. P. Lang, *J. Am. Chem. Soc.*, **83**, 2085 (1961), and other papers cited therein.

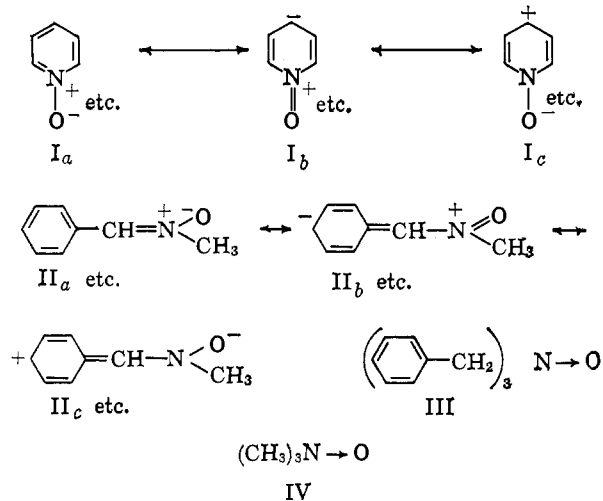
(5) (a) E. Ochiai, *J. Org. Chem.*, **18**, 534 (1953); (b) H. H. Jaffé and M. Orchin, "Theory and Applications of Ultraviolet Spectroscopy," John Wiley and Sons, Inc., New York, N. Y., 1962, p. 381; (c) T. Kubota, *J. Spectroscop. Soc. Japan*, **10**, 83 (1962).

(6) T. Kubota and M. Yamakawa, *Bull. Chem. Soc. Japan*, **36**, 1564 (1963).

(7) (a) T. D. Stewart and S. Maeser, *J. Am. Chem. Soc.*, **46**, 2583 (1924); (b) P. Nylén, *Tidsskr. Kemi Bergvesen*, **18**, 48 (1938); (c) M. M. Davis and H. B. Hetzer, *J. Am. Chem. Soc.*, **76**, 4247 (1954).

(1) (a) This work was supported by a grant from the National Science Foundation, G-20375; (b) presented at the 146th National Meeting of the American Chemical Society, Denver, Colo., Jan. 22, 1964.

(2) On leave of absence from the Shionogi Research Laboratory, Fukushima-ku, Osaka, Japan.



dipole moment³ and longer N–O distance⁸ in the aliphatic type than for pyridine N-oxide, etc. In fact, compounds III and IV are very strong donors for boron trifluoride,⁹ sulfur dioxide,⁹ some dye molecules, etc.^{7c} In this paper the iodine complexing ability of the aliphatic and aromatic amine N-oxides will be investigated and compared.

Experimental

Pyridine N-Oxide. Pure pyridine N-oxide,¹⁰ synthesized and purified by Ochiai's method⁵ from pyridine and hydrogen peroxide, was further purified by vacuum distillation three times, and the middle portion (113–114°, 3–4 mm.) of the last distillate was used. This compound is a hygroscopic, white, solid crystal, m.p. 68–69° of a carefully dried sample in a fused capillary.

N-Methylbenzaldoxime. Synthesized and purified N-methylbenzaldoxime reported previously^{3d} was further recrystallized twice with benzene–petroleum ether and was kept in a desiccator with P₂O₅ in the dark, m.p. 84°.

Trimethylamine N-Oxide. First, the dihydrate, (CH₃)₃NO·2H₂O, was prepared by neutralizing the pure HCl salt¹¹ (m.p. 218–218.5° dec.) with silver oxide–water mud by a well-known method and by recrystallizing three times from alcohol and ether.¹² This dihydrate, obtained as a prolonged colorless needle crystal, m.p. ~96°, was sublimed twice under a good vacuum system equipped with a liquid nitrogen trap to get the final anhydrous substance.¹² The anhydrous compound is a hygroscopic white crystal

(8) (a) A. Caron, G. J. Palenik, E. Goldish, and J. Donohue, *Acta Cryst.*, **17**, 102 (1964); (b) A. Caron and J. Donohue, *ibid.*, **15**, 1052 (1962); (c) C. Rezat, *ibid.*, **13**, 63 (1960); (d) G. Tsoucaris, *ibid.*, **14**, 14 (1961); (e) Y. Namba, T. Oda, H. Itoh, and T. Watanabe, *Bull. Chem. Soc. Japan*, **33**, 1618 (1960); (f) Y. Namba, T. Oda, and T. Watanabe, *ibid.*, **34**, 889 (1961); (g) E. L. Eichhorn, *Acta Cryst.*, **12**, 746 (1959); (h) K. Folting and W. N. Lipscomb, *ibid.*, **17**, 1263 (1964).

(9) (a) A. B. Burg, *J. Am. Chem. Soc.*, **65**, 1629 (1943); (b) H. Z. Lecher and W. B. Hardy, *ibid.*, **70**, 3789 (1948); (c) A. B. Burg and J. H. Bickerton, *ibid.*, **67**, 2261 (1945).

(10) This compound was supplied by Professor Y. Mori, Osaka Gakugei University, Japan, to whom the author's thanks are due.

(11) This was supplied by Mr. H. Miyazaki, Shionogi Research Lab., and it was prepared from the dihydrate (the first class grade of Kanto Kagaku Co., Ltd.) and HCl, and then recrystallized four times from methanol. The author's thanks are due to him.

(12) J. Meisenheimer, *Ann.*, **397**, 286 (1913); W. A. Noyes and J. H. Hibben, *J. Am. Chem. Soc.*, **45**, 355 (1923); W. R. Dunstan and E. Goulding, *J. Chem. Soc.*, **75**, 1004 (1899), etc.

which melts with sublimation at 190–192° using a fused capillary to prevent contamination by moisture.¹³ Infrared spectra of the anhydride, dihydrate, and HCl salt of trimethylamine N-oxide agree well with the patterns in the literature.¹⁴ The anhydrous compound was kept in a desiccator with P₂O₅ in the dark.

Tribenzylamine N-Oxide. This compound was synthesized and purified at room temperature by the method of Davis and Hetzer^{7c} from a glacial acetic acid solution of tribenzylamine (Eastman Organic Chemicals, pure grade, once recrystallized from ethanol) and 30% hydrogen peroxide. The N-oxide thus obtained was thoroughly washed with chilled water, sufficiently dried, washed again with excess benzene, and filtered. The final product (m.p. 123 ± 0.5° dec.) was dried at room temperature under high vacuum with P₂O₅ desiccant. The absorption spectrum in alcohol and the melting point range are consistent with the data of the literature.^{7c} An infrared spectrum by the Nujol mull method shows the N–O stretching frequency at 930–935 cm.⁻¹ with a strong intensity. This sample stored in a desiccator with P₂O₅ was kept in the refrigerator to prevent thermal decomposition.^{7c, 15}

Iodine. Fisher Certified iodine (resublimed) was reperfired by subliming twice under a nitrogen atmosphere and was kept in a desiccator with calcium chloride protected from the light.

Purification of carbon tetrachloride was followed by the method recommended by Weissberger and Proskauer.¹⁶ Fisher Certified carbon tetrachloride was first refluxed over pure mercury, then washed with 20% aqueous NaOH solution, water, concentrated H₂SO₄, NaOH solution, and again with water. It was dried over fused calcium chloride and distilled using a Podbielniak column from fresh calcium chloride in a system protected from atmospheric moisture. Spectroanalyzed dichloromethane purchased from Fisher Scientific Co. was dried with Drierite and distilled with a Podbielniak column in a system protected from moisture. These solvents were used, because non-polar solvents such as *n*-heptane, etc., which are preferable, dissolved only a small amount of I, II, III, and IV, so that the determination of the exact concentration was difficult. Therefore carbon tetrachloride was employed as solvent for I and II, and dichloromethane was used for III and IV.

A Beckman Model DK-2 spectrophotometer equipped with a Beckman temperature-regulated cell holder was used for measuring absorption spectra. A temperature constant within ±0.5° was maintained by circulating water from a thermostat through the cell holder. Dry nitrogen gas was flushed through the spectrophotometer during the recording of spectra below room temperature to prevent the condensation of atmospheric moisture on the cell windows and other optics located nearby. Purified solvents were stocked

(13) These values are not very accurate and sometimes melting occurs at ~205°. This is due to the sublimation which makes it difficult to determine the melting point.

(14) (a) P. A. Giguere and D. Chin, *Can. J. Chem.*, **39**, 1214 (1961); (b) D. Cook, *ibid.*, **41**, 1127 (1963); (c) Y. Matsui and T. Kubota, *J. Chem. Soc. Japan, Pure Chem. Sect.*, **83**, 985 (1962).

(15) It was found that another purified tribenzylamine N-oxide, obtained as a colorless crystal by concentrating the dichloromethane solution at room temperature and drying in a desiccator with P₂O₅ under vacuum, has the same physical constants.

(16) A. Weissberger and E. Proskauer, "Organic Solvent," 2nd Ed., Interscience Publishers, Inc., New York, N. Y., 1956.

in a bottle, which was connected to a commercial automatic buret provided with calcium chloride tubes. This buret was always operated with N₂ gas led through the calcium chloride tube. Also, to minimize hydration effects on the experimental results, the volumetric flasks, pipets, and absorption cells, etc., were flushed by a jet of N₂ gas before use. The sampling of the trimethylamine oxide was always carried out in a drybox. Since N-oxides except for II are hygroscopic, the following special precautions were taken in weighing the sample. A suitable quantity of sufficiently dried N-oxides was first inserted quickly in a 50-ml. volumetric flask of known weight, and this flask was kept in a desiccator with P₂O₅ under vacuum. After 2 days dry air was led through a liquid N₂ trap and CaCl₂ tube; then the flask including the sample was weighed. The accurate weight of the samples was obtained by subtracting the weight of the empty flask. The stock solutions of the amine oxides were freshly prepared on the day of measurement and kept in a dark place except during sampling. All the measurements of the spectra were made within 40 min. after preparation of the mixed solutions. Usually the cells used are 1-cm. matched quartz cell equipped with stoppers. A matched quartz cell of 5 cm. was used for measurement of the shifted iodine band of I and II. This makes it possible to employ dilute iodine solutions, which are very suitable conditions for deriving eq. 2 mentioned later. On the other hand, nearly matched quartz cells of lengths 0.01 and 0.027 cm. were also used to study the spectral behavior in the ultraviolet region, because I, etc., show strong absorption ($\epsilon > 10^4$) in the near-ultraviolet region. In addition, a thin cell is useful to extend the recording region to much shorter wave lengths. The above thin cells were made by inserting a quartz spacer in the matched 1.00-cm. cell. Throughout the present work, special care was taken to ensure that the same spacer was always inserted in the same cell of the matched pair (1.00 cm.), the same cell having the same spacer being used for the reference solution, and that the same surfaces of the cells and spacers faced the incident light beam. The evaporation of the solvent was prevented by first putting the usual glass cell cover on the cell top, and again the cell was doubly covered by the contact aluminium cell cover. Under these conditions, reproducible results were obtained. It is, however, important to remove carefully small bubbles which occasionally attach in the thin layer.¹⁷ The cell length of the thin cells was decided by comparing the absorption intensity of the N-oxides with one estimated using the usual 1.00-cm. matched cell.

Stability of the Complexes. Under the concentration employed here, the iodine complex of pyridine N-oxide is stable. No change of the solution color and no precipitation were visually found for over 7 days. However, we could find that the intensity of the shifted iodine spectrum increases a little at the wave length region less than 400 m μ after standing more than 24 hr. This phenomenon may be due to the formation of a very small quantity of I₃⁻ ion as mentioned later. The tendency to change is greater for the iodine complex of N-methylbenzaloxime. After standing over-

(17) The height of the spectra is lower than the 1-cm. cell, so that spacers were covered completely by solutions.

night, the solution color varied to a more yellowish hue, and sometimes a very fine brownish precipitation was found on the wall of the flask. Even if mixed solutions (10⁻³–10⁻² mole/l.) of relatively high concentration were prepared, however, the solution of the complex is stable for 1 hr., especially at lower temperatures. For this compound the complex formation seems also to accelerate gradually the chemical change at the bond $>C=N<$ on reference to the results in acidic (HCl) aqueous solutions, where the N-methylbenzaloxime is relatively unstable and shows the change indicating the above bond to be the reaction center.⁶ For the iodine complexes of the aliphatic amine oxides III and IV, no change of the solution color and no precipitation were visually found in the dichloromethane solution even after 24 hr. under the experimental conditions studied here. However, as in the case of the pyridine N-oxide–iodine complex, a small increase in intensity in the wave length region (less than 390 m μ) was found with the lapse of time, this change being slow at lower temperature. This instability of the trimethylamine N-oxide–iodine complex is larger than that of the tribenzylamine N-oxide–iodine complex. For example, the mixed solution of trimethylamine N-oxide (1.504 \times 10⁻⁴ mole/l.) and iodine (5.185 \times 10⁻⁵ mole/l.) in dichloromethane clearly exhibits the shoulder band at about 290 m μ , which corresponds to the I₃⁻ ion, after standing for 1 day, and at the same time the decrease in intensity was found in the charge-transfer (C.T.) band (257 m μ) seen in Figure 10. These results show I₃⁻ to be produced with the lapse of time in the mixed solution. The main reasons for this phenomenon seem to be due to the fact that the solvent CH₂Cl₂ is somewhat polar (the dielectric constant is 9.08 at 20°), original N-oxides are also very polar, and the complex is quite strong. It is worthwhile to point out that the formation of the I₃⁻ ion is accelerated by irradiation of the light corresponding to the absorption spectrum of the I₃⁻ ion.

Results

Shifted Iodine Band and Determination of Thermodynamic Constants. As is shown in Figures 1–4, it was clearly observed that the visible iodine band having an absorption maximum at 520 m μ in carbon tetrachloride and at 506 m μ in dichloromethane is shifted to shorter wave length by adding a small quantity of N-oxides, and that there is a fine isosbestic point. These results indicate that a 1:1 molecular complex of iodine with N-oxide is formed in mixed solution and that this complex is in equilibrium, as is expressed by eq. 1, with free iodine and free N-oxide.

$$K = C_{DA}/(C_D^0 - C_{DA})(C_A^0 - C_{DA}) \quad (1)$$

Here, C_D⁰ and C_A⁰ are, respectively, the total concentrations (moles/l.) of N-oxide and iodine, and C_{DA} is that of the 1:1 complex. If it is possible to assume the condition C_D⁰ \gg C_A⁰ and no light absorption due to the N-oxide at the wave length used to calculate the equilibrium constant K, we can easily derive eq. 2 by applying the relation C_A⁰($\epsilon - \epsilon_A$) = C_{DA}($\epsilon_{DA} - \epsilon_A$), where ϵ_A and ϵ_{DA} are the molecular extinction coefficients of the free iodine and the complex (DA), respectively, and ϵ is the apparent molecular extinction coefficient calculated using concentration C_A⁰. Equa-

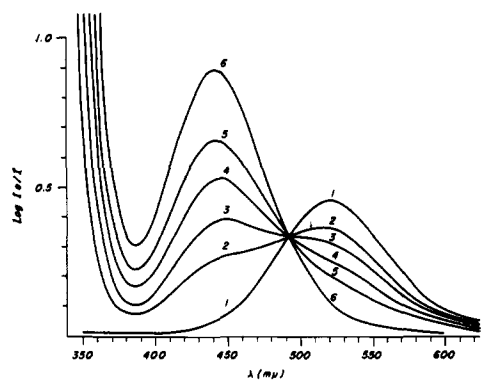


Figure 1. The visible absorption spectra of iodine-pyridine N-oxide in CCl_4 (23° , 5-cm. cell): curve 1 is for iodine ($9.550 \times 10^{-5} M$); the concentrations of pyridine N-oxide are $4.210 \times 10^{-3} M$ for curve 2, $8.421 \times 10^{-3} M$ for curve 3, $16.84 \times 10^{-3} M$ for curve 4, and $33.68 \times 10^{-3} M$ for curve 5; curve 6 is for the absorption due solely to the complexed iodine molecule.

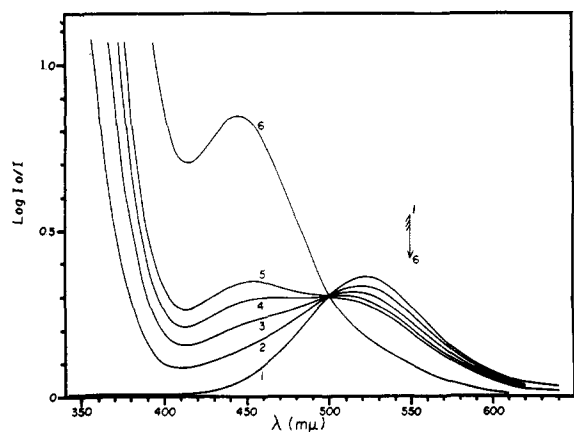


Figure 2. The visible absorption spectra of iodine-N-methylbenzaldoxime in CCl_4 : (15° ; 5-cm. cell): curve 1 is for iodine ($7.502 \times 10^{-5} M$); the concentrations of N-methylbenzaldoxime are $3.794 \times 10^{-3} M$ for curve 2, $7.588 \times 10^{-3} M$ for curve 3, $11.38 \times 10^{-3} M$ for curve 4, and $15.18 \times 10^{-3} M$ for curve 5; curve 6 is for the absorption due solely to the complexed iodine molecule.

tion 2 indicates a linear relation of ϵ to $(\epsilon_A - \epsilon)/C_D^0$, and K and ϵ_{DA} can be directly evaluated from the slope

$$\epsilon = \frac{1}{K} \left(\frac{\epsilon_A - \epsilon}{(C_D^0)^2} \right) + \epsilon_{DA} \quad (2)$$

and the intercept at the vertical axis even if the free iodine and shifted iodine bands overlap at the wavelength adopted to calculate K .^{18,19} This method was safely applied to the analysis of the experimental results with I and II. As an example, in Figure 5 is shown the linear relationship of eq. 2 obtained from the experimental results for the pyridine N-oxide-iodine complex. The same good linear relationship was also obtained for the N-methylbenzaldoxime-iodine complex. K and ϵ_{DA} thus evaluated are shown

(18) From this point of view, eq. 2 seems to be very convenient, although another form was introduced by J. A. A. Ketelaar, *et al.*, *Rec. trav. chim.*, 71, 1104 (1952).

(19) Here it should be noted that the small variation of concentrations owing to the temperature change was corrected using data on the temperature dependence of the density of pure solvents cited from "The International Critical Tables," Vol. III, McGraw-Hill Book Co., Inc., New York, N. Y., 1930, p. 27, for CCl_4 ; and Landolt-Börnstein, "Zahlenwerte und Funktionen 6," Vol. II, Part 2, Springer-Verlag, Berlin, 1960, p. 185, for CH_2Cl_2 .

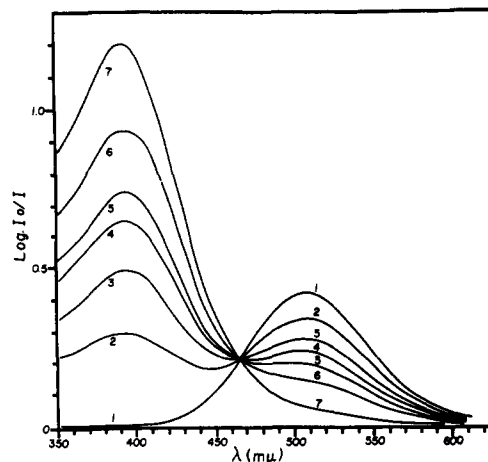


Figure 3. The visible absorption spectra for the three-component system of tribenzylamine N-oxide + iodine + dichloromethane (solvent) (cell length, 1 cm.; 20°): the concentration of iodine is $4.618 \times 10^{-4} M$; the concentrations of N-oxide are 0 for curve 1, $2.043 \times 10^{-4} M$ for curve 2, $4.086 \times 10^{-4} M$ for curve 3, $6.129 \times 10^{-4} M$ for curve 4, $8.172 \times 10^{-4} M$ for curve 5, and $14.301 \times 10^{-4} M$ for curve 6; curve 7 is for the absorption due solely to the complexed iodine molecule.

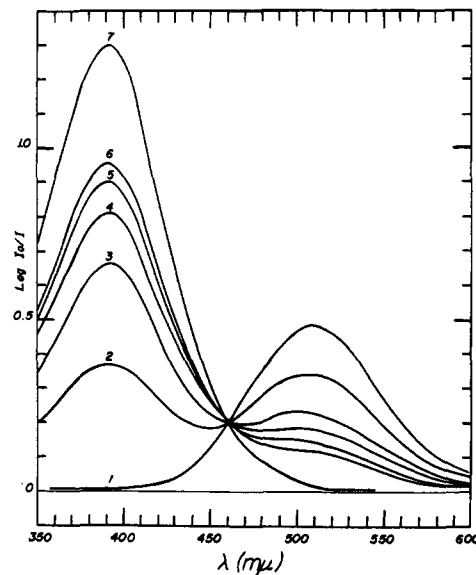


Figure 4. The visible absorption spectra for the three-component system of trimethylamine N-oxide + iodine + dichloromethane (solvent) (cell length, 1 cm.; 22°): the concentration of iodine is $5.200 \times 10^{-4} M$; the concentrations of N-oxide are 0 for curve 1, $1.848 \times 10^{-4} M$ for curve 2, $3.696 \times 10^{-4} M$ for curve 3, $4.620 \times 10^{-4} M$ for curve 4, $5.544 \times 10^{-4} M$ for curve 5, and $6.468 \times 10^{-4} M$ for curve 6; curve 7 is for the absorption due solely to the complexed iodine molecule.

in Table I. On the other hand, for the case of the compounds III and IV, the equilibrium constant is quite large, and the molecular complex is formed at comparable concentrations of iodine and N-oxides as in Figures 3 and 4. We cannot apply the Benesi-Hildebrand equation,²⁰ its modified form,²¹ or eq. 2. Since the absorption of the III, IV, and iodine are very small in the wavelength region from 400 to 350 μm , the optical densities owing to each component of the

(20) H. A. Benesi and J. H. Hildebrand, *J. Am. Chem. Soc.*, 71, 2703 (1949).

(21) R. L. Scott, *Rec. trav. chim.*, 75, 787 (1956).

Table I. Equilibrium Constants Obtained at Different Wave Lengths and Temperatures

Wave length, $m\mu$	K , l./mole				ϵ , l./mole cm.			
	7°	15°	23°	33°	7°	15°	23°	33°
Pyridine N-Oxide (Solvent, CCl_4)								
440	134	106	78.9	56.5	1880	1850	1860	1840
425	127	101	74.0	52.6	1670	1640	1650	1640
450	137	109	80.6	58.6	1800	1780	1800	1760
Average	133	105	77.9	55.9				
N-Methylbenzaloxime (Solvent, CCl_4)								
450 ^a		5°	15°	28°	5°	15°	28°	
		47.3	35.8	23.4	2320 ^b	2300 ^b	2280 ^b	
Tribenzylamine N-Oxide (Solvent, CH_2Cl_2)								
		20°	12°	4°	20 ^b	12 ^b	4 ^b	
390		3420	5710	10200	2550	2420	2310	
380		3490	5530	9750	2410	2400	2250	
400		3500	5340	9800	2490	2430	2300	
Average		3470	5520	9920	
Trimethylamine N-Oxide (Solvent, CH_2Cl_2)								
		22°	13°	6.5°	22 ^b	13 ^b	6.5 ^b	
390		5770	9850	15000	2800	2760	2700	
400		5670	9500	13500	2790	2700	2600	
380		5550	9200	15300	2740	2660	2590	
Average		5660	9520	14600	

^a This wave length corresponds to that where the largest variation of the optical density occurred in the spectra (see Figure 2). ^b These values are overlapped more or less with the C.T. absorption band.

complex can be safely neglected in the said wave length region. The well-known eq. 3 was used to evaluate the equilibrium constant K .²² Here, D is

iterative plotting, we are able to get the final ϵ_{DA} and K values. First, the evaluation of ϵ_{DA} and also K was made by the method of least squares using observed

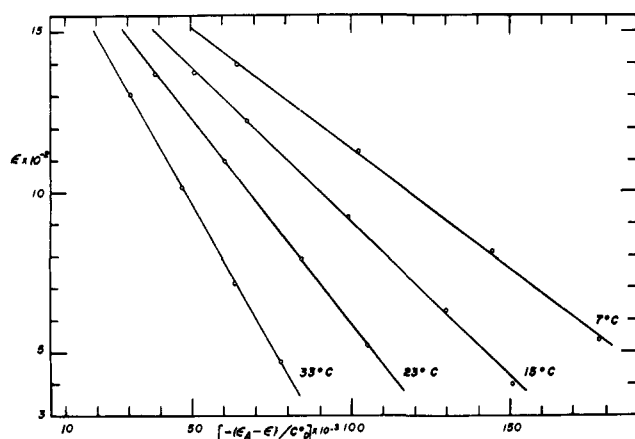


Figure 5. The linear relationship between ϵ and $(\epsilon_A - \epsilon)/C_D^0$ in eq. 2 at $440 m\mu$ and at various temperatures for the system iodine-pyridine N-oxide- CCl_4 (solvent).

the optical density at a certain wave length and other notations have the same meaning as in eq. 1 and 2.

$$\frac{C_D^0 C_A^0}{D} = \frac{1}{\epsilon_{DA}} \left(C_D^0 + C_A^0 - \frac{D}{\epsilon_{DA}} \right) + \frac{1}{\epsilon_{DA} K} \quad (3)$$

As was previously pointed out by Lang,²² if we can estimate ϵ_{DA} using another method, the plotting of $C_D^0 C_A^0 / D$ against $(C_D^0 + C_A^0 - D/\epsilon_{DA})$ should be led to a linear relation with slope $1/\epsilon_{DA}$ and intercept $1/K\epsilon_{DA}$ which lead to a new ϵ_{DA} and K . Using this ϵ_{DA} a new set of ϵ_{DA} and K is again decided, and after this

(22) R. P. Lang, *J. Am. Chem. Soc.*, **84**, 1185 (1962).

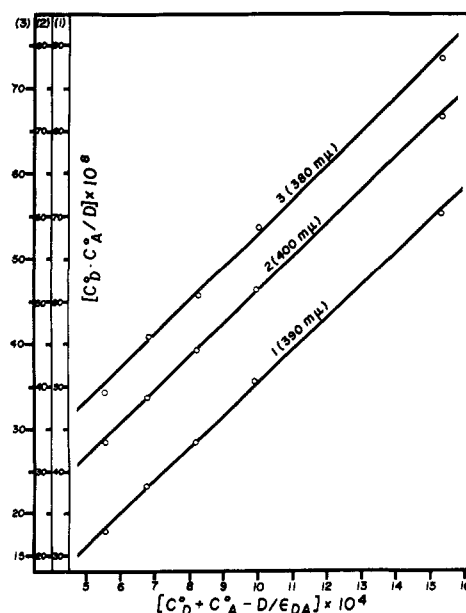


Figure 6. The linear relationship between $(C_D^0 + C_A^0 - D/\epsilon_{DA})$ and $C_D^0 C_A^0 / D$ at 20° and at various wave lengths for the system tribenzylamine N-oxide + iodine + dichloromethane. The vertical scales 1, 2, and 3 should be referred to straight lines 1, 2, and 3, respectively.

optical densities, the details of which were written in Briegleb's book.²³ The plotting of $C_D^0 C_A^0 / D$ vs. $(C_D^0 + C_A^0 - D/\epsilon_{DA})$ using ϵ_{DA} thus obtained led to a good linear relation, and repeated plottings gave al-

(23) G. Briegleb, "Elektronen-Donator-Acceptor-Komplexe," Springer-Verlag, Berlin, 1961, p. 210 ff.

Table II. The Thermodynamic and Spectral Characteristics of the Iodine Molecular Complexes with Tertiary Amine N-Oxides

Base (solvent)	ΔH , kcal./mole (ΔS , e.u.)	Shifted I ₂ band	C.T. band	Absorption band of donor itself	End absorption ^c
Pyridine N-oxide (CCl ₄)	-5.85 ± 0.3 (-11.0 ± 0.5)	λ_{\max} 441 m μ ϵ_{\max} 1860 (23°) $f = 0.0326$ $\Delta\bar{\nu}_{1/2} = 4060 \text{ cm.}^{-1}$ $D = 1.75 \text{ D.}$	λ_{\max} 318.4 m μ ϵ_{\max} 25,600 $f = 0.506$ $\Delta\bar{\nu}_{1/2} = 4580 \text{ cm.}^{-1}$ $D = 5.85 \text{ D.}$	In free donor λ_{\max} 284.4 m μ ϵ 16,000 In complex $\lambda_{\max} \sim 278 \text{ m}\mu$ $\epsilon \sim 10,000$	<245 m μ
N-Methylbenzaloxime (CCl ₄)	-5.25 ± 0.5 (-11.2 ± 0.5)	λ_{\max} 446 m μ ϵ_{\max} 2180 (15°) a $f = 0.039$ $\Delta\bar{\nu}_{1/2} = 4190 \text{ cm.}^{-1}$ $D = 1.93 \text{ D.}$	λ_{\max} 342.5 m μ ϵ_{\max} 25,500 $f = 0.531$ $\Delta\bar{\nu}_{1/2} = 4826 \text{ cm.}^{-1}$ $D = 6.21 \text{ D.}$	In free donor λ_{\max} 301 m μ ϵ 19,800 In complex $\lambda_{\max} \sim 286 \text{ m}\mu$ $\epsilon \sim 14,000$	<260 m μ
Tribenzylamine N-oxide (CH ₂ Cl ₂)	-10.5 (-19.6)	λ_{\max} 393~394 m μ ϵ_{\max} 2580 (20°) ^a $f = 0.054^a$ $\Delta\bar{\nu}_{1/2} = 4860 \text{ cm.}^{-1a}$ $D = 2.12 \text{ D.}^a$	λ_{\max} 268 m μ ϵ_{\max} 31,000 $f = 0.993$ $\Delta\bar{\nu}_{1/2} = 7420 \text{ cm.}^{-1}$ $D = 7.52 \text{ D.}$		
Trimethylamine N-oxide (CH ₂ Cl ₂)	-10.0 (-16.9)	λ_{\max} 391~392 m μ ϵ_{\max} 2810 (22°) ^b $f = 0.058^b$ $\Delta\bar{\nu}_{1/2} = 4750 \text{ cm.}^{-1b}$ $D = 2.19 \text{ D.}^b$	λ_{\max} 257 m μ ϵ_{\max} 30,700 $f = 0.805$ $\Delta\bar{\nu}_{1/2} = 6070 \text{ cm.}^{-1}$ $D = 6.64 \text{ D.}$		

^a This band seems more or less to be overlapped with the tail of the C.T. band. It was here assumed for the evaluation of these quantities that the shorter wave length side absorption curve against the band peak is symmetrical in cm.⁻¹ to that of longer side absorption, where the overlap is very small. ^b These values were derived by the method similar to a. The direct evaluation from the recorded curve led to the values $\Delta\bar{\nu}_{1/2} = 6211 \text{ cm.}^{-1}$, $f = 0.075$, and $D = 2.50 \text{ D.}$ ^c See text.

most the same value. In Figure 6 are shown some examples of this plotting at various wave lengths for the system of the iodine complex with tribenzylamine N-oxide, where large changes of the optical densities were found. The same linear relations were also obtained for the complex with IV. The final values of K and ϵ_{DA} were included in Table I.²⁴ In Figures 1-4 the spectrum due solely to the complexed iodine molecule is also given. These were calculated on the basis of the concentrations of the complex obtained using K and ϵ_{DA} stated before. From this spectrum we have calculated the oscillator strength f , transition moment D , etc., using the formula given by Tsubomura and Lang.^{4,25} Here the approximation, $\int \epsilon d\bar{\nu} = \epsilon \Delta\bar{\nu}_{1/2}$ ($\Delta\bar{\nu}_{1/2}$ is the half-width of the band in cm.⁻¹), was adopted. The results are collected in Table II, in which are also included the heat of formation ΔH (kcal./mole) and the entropy change ΔS (e.u.) owing to the complex formation. These were obtained by the standard method from a plot of $R \ln K$ vs. $1/T$, which led to a good straight line. The uncertainty in ΔH for the complexes with III and IV was determined to be about 1 kcal./mole by making an estimate of the uncertainty in the K values. A small increase of ϵ_{DA} , seen in Table I, with increasing temperatures may be due to the slight contribution from I₃⁻ ion as was stated in the Experimental section, and the ΔH values in Table II are a little overestimated, because such a change of ϵ_{DA} gives rise to an additional increase of the change of K by the temperature difference.

The Behavior of the Near-Ultraviolet Spectra as Affected by Complex Formation. Pyridine N-oxide

(24) It was found that the experiments made above 30° do not give the good results expected from eq. 3, and that reliable results are not obtained. This seems to be due to the large vaporization because of the low boiling point (39.9°) of CH₂Cl₂ and the contamination from the I₃⁻ ion which may disturb the results somewhat.

(25) R. S. Mulliken and W. B. Person, *Ann. Rev. Phys. Chem.*, 13, 107 (1962).

and N-methylbenzaloxime in nonpolar solvents show strong bands ($\epsilon > 10,000$) in the near-ultraviolet. These prevent the use of 1-cm. cells to study the spectral behavior in that region, because if we use a 1-cm. cell to record the C.T. spectra, very dilute solution of N-oxides (less than 10⁻⁴ mole/l.) must be employed, so that iodine solution of a high concentration is necessarily required on the basis of the K listed in Table I. This is not acceptable since continuous absorption due to I₂ and I₄ appears in the near-ultraviolet with considerable intensity. However, this defect could be removed by using a thin cell. In addition we could extend the recording region to even shorter wave length than in the case of a 1-cm. cell. In Figures 7 and 8 is shown the behavior of the ultraviolet spectra of pyridine N-oxide and N-methylbenzaloxime as affected by complex formation. We can see from these figures that the new bands, the maxima of which are at 318.4 and 342.5 m μ for pyridine N-oxide and N-methylbenzaloxime, respectively, occur at considerably longer wave lengths than the absorption maximum of the free N-oxide, while at the same time the intensity of light absorption in a shorter wave length region than that of free N-oxide band is also increased, and that two isosbestic points can be found in each figure. If these spectral changes are due to complex formation, the equilibrium constant K obtained from the spectral behavior in Figures 7 and 8 should coincide with that obtained from shifted iodine bands. Unfortunately, under the experimental conditions for the thin cell used here, the relation $C_D \ll C_A^0$ or $C_D \gg C_A^0$ is not satisfied. We cannot apply the eq. 2. Then we will use eq. 3. Now ϵ_{DA} was firstly estimated using the observed intensity and the K in Table I. For example, this plotting at 318.4 and 342.5 m μ , where the absorption intensity of free N-oxide is zero or negligible for pyridine N-oxide and N-methylbenzaloxime, re-

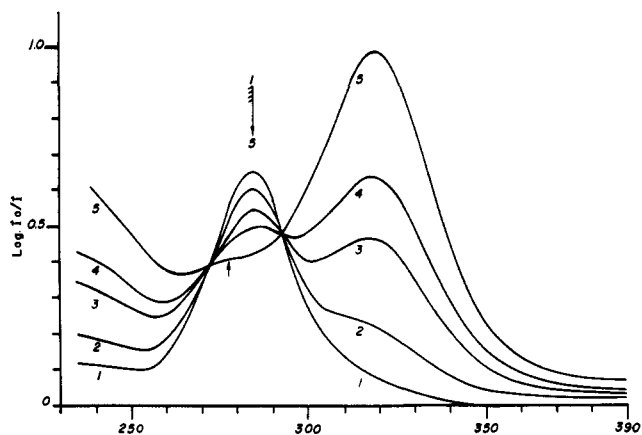


Figure 7. The ultraviolet absorption spectra of iodine-pyridine N-oxide solution (solvent CCl_4 , 23° , 0.01-cm. cell): curve 1 is for pyridine N-oxide $3.870 \times 10^{-3} M$; concentrations of iodine are $2.804 \times 10^{-3} M$ for curve 2, $11.218 \times 10^{-3} M$ for curve 3, and $22.435 \times 10^{-3} M$ for curve 4; curve 5 is for the absorption due solely to the complex molecule. In the case of curves 2, 3, and 4, the iodine solution corresponding to the free iodine concentration, which was estimated on the basis of the K decided from the shifted iodine band, was used as reference to cancel the absorption owing to the free iodine.

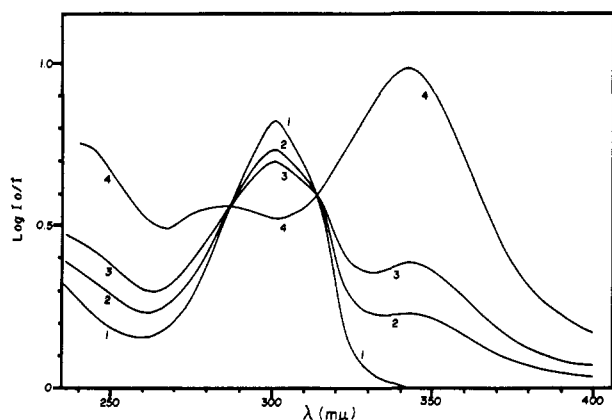


Figure 8. The ultraviolet absorption spectra of iodine-N-methylbenzaloxime solution (solvent CCl_4 , 15° , 0.01-cm. cell): curve 1 is for N-methylbenzaloxime $3.746 \times 10^{-3} M$; concentrations of iodine are $9.251 \times 10^{-3} M$ for curve 2 and $18.50 \times 10^{-3} M$ for curve 3; curve 4 is for the absorption due solely to the complex molecule. In the case of curves 2 and 3, the iodine solution corresponding to the free iodine concentration, which was estimated on the basis of the K decided from the shifted iodine band, was used as reference to cancel the absorption owing to the free iodine.

spectively, led to a good straight line, and finally the following ϵ_{DA} and K values were obtained: $\epsilon_{\text{DA}} = 25,600$ and $K = 74.4$ (at 23°) for pyridine N-oxide, and $\epsilon_{\text{DA}} = 25,500$ and $K = 40.0$ (at 15°) for N-methylbenzaloxime. The accuracy of these values, however, is less than that of those obtained from the shifted iodine band. This is dependent on the experimental conditions; that is, the reference cell containing I_2 solution corresponding to free I_2 concentration was filled to cancel the contribution from the absorption due to the free I_2 and a small quantity of I_4 species, which were calculated on the basis of the K obtained from the shifted I_2 band. In Figure 9 is shown the C.T. spectra recorded at 20° and using a 1-cm. cell with the mixed solutions of tribenzylamine N-oxide and iodine in dichloromethane. The same spectra were also re-

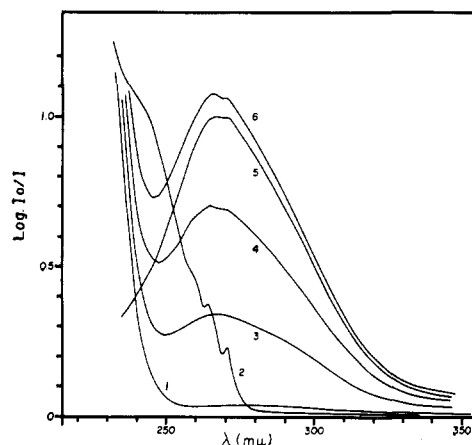


Figure 9. The ultraviolet absorption spectra recorded at 20° and using a 1-cm. cell with mixed solutions of tribenzylamine N-oxide and iodine in dichloromethane: the iodine concentration is $4.870 \times 10^{-4} M$; the concentrations of N-oxide are 0 for curve 1, $1.761 \times 10^{-6} M$ for curve 3, $3.523 \times 10^{-6} M$ for curve 4, and $5.284 \times 10^{-6} M$ for curve 6; curve 2 is for the absorption of tribenzylamine N-oxide of the concentration $1.761 \times 10^{-4} M$; curve 5 is for the spectrum due solely to the complex itself.

corded using 0.027-cm. cells. Since tribenzylamine N-oxide absorbs the light from 280 $m\mu$ to shorter wave length (curve 2 in Figure 9), the recorded C.T. band overlaps with this original donor band. Using the ϵ_{DA} and K from Table I, the iterative plotting of eq. 3 gave a good straight line, and finally the following ϵ_{DA} and K values were obtained at 20° and 270 $m\mu$; $K = 3000$ and 3320, and $\epsilon_{\text{DA}} = 34,300$ and 30,600 from the experiments using the 0.027- and 1-cm. cells, respectively. The K values here obtained are almost the same as in Table I. The absorption spectra due solely to the complex itself drawn in Figures 7-9 were arrived by subtracting the optical densities for the free N-oxide and free iodine and by converting the intensity into that of the total N-oxide concentration. In Table II various spectral data are given on these new bands estimated by the same method as that of the shifted iodine band. It should be noted that the maximum of the C.T. spectrum of I_2 complex with tribenzylamine N-oxide has two small humps, the positions of which almost coincide with ones of small maxima appearing in the spectrum of original N-oxide. It is conceivable that since the functional group for the complex formation is clearly the oxygen atom in $\text{N} \rightarrow \text{O}$ group, the $n \rightarrow \sigma^*$ transition of which appears at much shorter wave length,²⁶ and the benzene rings in the molecule are insulated by the $-\text{CH}_2-$ bridge, the absorption of the donor itself in the complex is almost the same as in a free state. Therefore, the humps seen in the C.T. band may be due to the absorption of the benzene part in the complex although their intensity seems to be small. In Figure 10 are shown the C.T. spectra of the trimethylamine N-oxide-iodine complex in dichloromethane recorded using 0.027-cm. cells under the conditions described in the figure. The spectra recorded using the 1-cm. cell gave also the same ones as in Figure 10, except that the isobestic point existing at 229.7 $m\mu$ could not be found because of a rapid increase in intensity of the light absorption of the solvent. The iterative plotting of eq. 3 on the basis of

(26) To be published later in detail.

the experiments similar to Figure 10 led to the values $\epsilon_{DA} = 33,600$ and $K = 5240$ at $260 \text{ m}\mu$, and other experiments covering the iodine concentrations $3\text{--}9 \times 10^{-4}$ mole./l. and N-oxide concentrations $1\text{--}16 \times 10^{-4}$ mole./l. gave almost the same K as that in Table I. The C.T. spectral data for trimethylamine N-oxide-iodine complex shown in Table II are average values obtained from the above experiments at 22° . The isosbestic point at $229.7 \text{ m}\mu$ seen in Figure 10 indicates that the contact C.T. spectrum due to the interaction between iodine and dichloromethane (curve 1) is decreased in intensity by the formation of stable complex, whose C.T. band appears at $257 \text{ m}\mu$. This is a reasonable result, because the stable complex formation brings about a decrease in the free iodine concentration which produces the contact charge-transfer interaction. Since the intensity of the C.T. band is very weak in the region of $220\text{--}230 \text{ m}\mu$ the N-V type spectrum due to the iodine itself in the complex seems to appear in the region below $220 \text{ m}\mu$.

Discussion

Complex Formation Ability on Tertiary Amine N-Oxides. As was stated in the Introduction, $2p\pi$ -electrons of the oxygen atom in pyridine N-oxide and N-methylbenzaldoxime are conjugated with the rest of the π -electron system, as has been verified by various experimental and theoretical studies.^{3,5,6,8,27,28} Although the net electronic charge at the oxygen atom is decreased by the above resonance effect, it must still be high because of the major contribution from the semipolar σ -bond ($\text{N}^+\text{--O}^-$); the main part of the dipole moment of pyridine N-oxide (4.19 D.) and N-methylbenzaldoxime (3.49 D.) may be doubtlessly caused by this σ -bond. In the case of tribenzylamine N-oxide and trimethylamine N-oxide there are no π -electron conjugated systems in the molecules, and the observed dipole moment for the latter is quite large (5.02 D.).³ Since the extra negative charge on the oxygen atom should make a better electron donor according to charge-transfer theory,^{25,29} the active donor center reasonably seems to be the oxygen atom. This conclusion is supported also by the fact that X-ray⁸ and infrared absorption studies of trimethylamine N-oxide and pyridine N-oxide HCl salts³⁰ show directly the presence of the hydrogen-bonded group $\text{N}\cdots\text{O}\cdots\text{H}\cdots\text{Cl}$. In addition, many reports on metal chelate complexes of pyridine N-oxide were recently published,³¹ where it was concluded that the oxygen atom participated in the bond formation to metals. Now it is especially of interest to compare ΔH and K values obtained from this research with those of other oxo compounds-iodine complexes. Table III shows that K and ΔH values of N-oxide-iodine complexes are much greater than those of other oxo compound-iodine complexes (see also Table III of

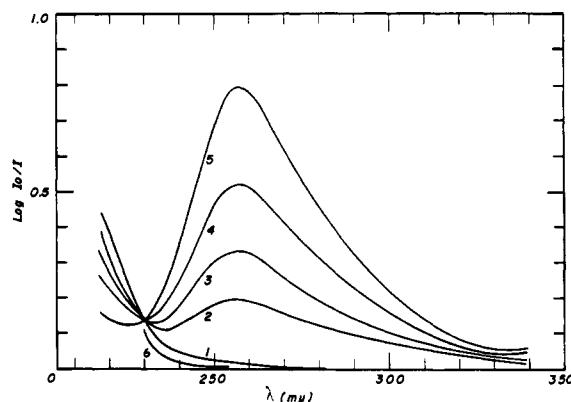


Figure 10. The ultraviolet absorption spectra recorded at 22° and using a 0.027-cm. cell with mixed solutions of trimethylamine N-oxide and iodine in dichloromethane; the iodine concentration is $9.550 \times 10^{-4} M$; the concentrations of N-oxide are 0 for curve 1, $2.162 \times 10^{-4} M$ for curve 2, $4.324 \times 10^{-4} M$ for curve 3, $8.648 \times 10^{-4} M$ for curve 4, and $15.136 \times 10^{-4} M$ for curve 5; curve 6 is for the absorption (1-cm. cell) due only to trimethylamine N-oxide, whose concentration is $8.507 \times 10^{-3} M$.

ref. 4); this indicates that the iodine-complexing ability of these N-oxides is stronger than for most oxo compounds. The complexing ability of aliphatic-type amine N-oxides especially is quite large. This is also indicated by the fact that the shifted iodine band maxima shown in Figures 3 and 4 and Table II appear at considerably shorter wave lengths than those observed for the other iodine complexes with various oxo compounds including the pyridine N-oxide, etc. That is, this blue shift is $\sim 112 \text{ m}\mu$, $\sim 16.05 \text{ kcal./mole}$, and $\sim 114 \text{ m}\mu$, $\sim 16.4 \text{ kcal./mole}$, for the iodine complexes with tribenzylamine N-oxide and trimethylamine N-oxide, respectively. These values are much larger than in other oxo compounds, and it is reasonable that the larger the blue shift of the visible iodine band is the stronger the iodine complex.^{22,32} Here it may also be noted that the acid dissociation constant^{5c,33} of pyridine N-oxide is much larger than that of compounds such as alcohols, ethers, ketones, etc., but it is much smaller than that⁷ of compounds III and IV, as is seen in Table III. Thus we can say that there is a parallel relation between pK_a and iodine-complexing ability of electron donors, as was pointed out by other authors on other systems.³⁴ Since protonation (pK_a) of an electron donor is considered to be the extreme case for hydrogen bonding, the relationship among ΔH , K , and pK_a suggests a similarity of mechanism between hydrogen bonding and iodine complexing where the charge-transfer force undoubtedly plays an important role. We can expect the aliphatic-type amine oxides will be especially good proton acceptors in hydrogen bonding, because the greater electron accumulation at the oxygen atom than in the case of pyridine N-oxide, etc., will increase both the charge-transfer force and electrostatic force. This situation, for example, is

(27) H. H. Jaffé, *J. Am. Chem. Soc.*, **76**, 3527 (1954); **77**, 4445 (1955), etc.

(28) T. Kubota, *J. Chem. Soc. Japan, Pure Chem. Sect.*, **80**, 578 (1959); *Bull. Chem. Soc. Japan*, **35**, 946 (1962); T. Kubota and H. Watanabe, *ibid.*, **36**, 1093 (1963), etc.

(29) R. S. Mulliken, *J. Am. Chem. Soc.*, **74**, 811 (1952); *J. Phys. Chem.*, **56**, 801 (1952), etc.

(30) Y. Matsui and T. Kubota, *J. Chem. Soc. Japan, Pure Chem. Sect.*, **83**, 985 (1962).

(31) S. I. Shupack and M. Orchin, *J. Am. Chem. Soc.*, **86**, 586 (1964); S. Kida, J. V. Quagliano, J. A. Walmsley, and S. Y. Tyree, *Spectrochim. Acta*, **19**, 189 (1963).

(32) R. S. Mulliken, *Rec. trav. chim.*, **75**, 845 (1956); J. Ham, *J. Am. Chem. Soc.*, **76**, 3875 (1954); S. Nagakura, *ibid.*, **80**, 520 (1958); T. Kubota, *J. Chem. Soc. Japan, Pure Chem. Sect.*, **78**, 196 (1957), etc.

(33) H. H. Jaffé and G. O. Doak, *J. Am. Chem. Soc.*, **77**, 4441 (1955). The acid dissociation constant of II may be expected to be the same order of that of pyridine N-oxide. The former is relatively unstable in the aqueous solution of $\text{pH} < 2\text{--}3$, so that the exact pK_a was not measured in our study.

(34) V. G. Krishna and M. Chowdhury, *J. Phys. Chem.*, **67**, 1067 (1963); H. Tsubomura, *J. Am. Chem. Soc.*, **82**, 40 (1960), etc.

Table III. Thermodynamic Data on Typical I₂ Complexes with Oxo Compounds and the pK_a Values of Electron Donors

Donor	Solvent	K, l./mole (temp. °C.)	ΔH, kcal./mole	pK _a
Methanol ^a	CCl ₄	0.473 (20)	-1.90	-2.2 ^j
Ethanol ^a	CCl ₄	0.451 (20)	-2.10	-2.3 ^k
<i>t</i> -Butyl alcohol	<i>n</i> -Heptane ^b	0.885 (21.5) ^q
	CCl ₄ ^c	0.107 (25) ^q	-3.4	-3.8 ^l
Acetone ^{d,e}	CCl ₄	0.28 (30) ^d	..	<-1 ^{i,m}
		0.85 (25) ^e
Ethyl ether ^{a,b}	<i>n</i> -Heptane	1.16 (20)	-4.2	-3 to -3.61 ^{i,n}
		0.723 (21.5) ^q
1,4-Dioxane ^f	<i>n</i> -Heptane	1.40 (25)	-3.5	-3.2 to -3.4 ^{i,o}
		1.00 (25)
N,N-Dimethylacetamide ^g	CCl ₄	6.8 (25)	-3.9	..
			-4.0	-1.4 ^p
Pyridine N-oxide ^h	CCl ₄	77.9 (23)	-5.85	+0.78-0.79 ⁱ
N-Methylbenzaldoxime ^h	CCl ₄	35.8 (15)	-5.25	<+~1.0 ⁱ
Tribenzylamine N-oxide ^h	CH ₂ Cl ₂	3470 (20)	-10.5	+4.70 ⁱ
Trimethylamine N-oxide ^h	CH ₂ Cl ₂	5660 (22)	-10.0	+4.60 ⁱ

^a See Table III in ref. 4. ^b J. S. Ham, *J. Chem. Phys.*, **20**, 1170 (1952). ^c R. M. Keefer and L. J. Andrews, *J. Am. Chem. Soc.*, **77**, 2164 (1955). ^d H. Yamada and K. Kozima, *ibid.*, **82**, 1543 (1960). ^e R. S. Drago, B. Wayland, and R. L. Carlson, *ibid.*, **85**, 3125 (1963). ^f J. D. McCollough and I. C. Zimmermann, *J. Phys. Chem.*, **65**, 888 (1961). ^g R. S. Drago, D. A. Wenz, and R. L. Carlson, *J. Am. Chem. Soc.*, **84**, 1106 (1962). ^h This work. ⁱ See text. ^j N. C. Deno and M. J. Wisotsky, *J. Am. Chem. Soc.*, **85**, 1735 (1963). ^k P. D. Bartlett and W. F. Smith, Ph.D. Thesis of W. S., Harvard University, 1960. ^l N. C. Deno, T. Edwards, and C. Perizzolo, *J. Am. Chem. Soc.*, **79**, 2108 (1957). ^m S. Nagakura, A. Minegishi, and K. Stanfield, *ibid.*, **79**, 1033 (1957). ⁿ E. M. Arnett and C. Y. Wu, *ibid.*, **82**, 4999 (1960); **84**, 1684 (1962). ^o E. M. Arnett, "Advances in Physical-Organic Chemistry," Vol. 1, Interscience Publishers, Inc., New York, N. Y., 1963. ^p This value is for acetamide; see footnote *j*. ^q These values were approximately calculated from originally reported values using the relation $K_c = K_x V_s$ where K_c and K_x are equilibrium constants expressed as l./mole and mole fraction units, and V_s is the molar volume at 25° (0.1475 and 0.0968 l./mole for *n*-heptane and carbon tetrachloride, respectively).

similar to the proton acceptor ability of various amine derivatives on the type R₁R₂R₃N, discussed by Mulliken.³⁵ This concept is supported by the facts that the equilibrium constant (l./mole) measured at room temperature for the three-component system (CH₃)₃NO + phenol + CH₂Cl₂ (solvent) is very large^{26,36} (over 3000) in comparison with the value 146 (l./mole) at 26.7° for the system quinoline N-oxide + phenol + CCl₄ (solvent),³⁷ and that the red shift and the intensification of the phenol ¹L_b band by hydrogen bonding is also large.

Ultraviolet Absorption Spectra of the Complexes. First let us consider the nature of the spectral data on pyridine N-oxide and N-methylbenzaldoxime. As is seen from curve 5 in Figure 7, the ultraviolet absorption spectrum of the pyridine N-oxide-iodine complex consists of three bands: the first is the 318.4-mμ band with strong intensity, next is a weak hidden band (~278 mμ), and the last band seems to appear at wave lengths less than 245 mμ. The situation for the complexed N-methylbenzaldoxime band is almost the same, as shown in Figure 8 and Table II. We can now tentatively make two interpretations. First, the longest wave length band and the hidden band are, respectively, of the nature of C.T. band and the blue-shifted original band mentioned later. The shortest wave length band may be considered the modified shorter wave length band of donors, which also have

the strong absorption bands in the wave length region less than 240 mμ.^{3,6,6} Secondly, the one at longest wave length is the intensified and red-shifted original donor band, and the shortest wave length band is a C.T. band, which may be overlapped with the shorter wave length band of donors mentioned above. The hidden band is due to the intensified ¹B₁ band of the donor itself which was predicted theoretically in this region.²⁸ Unfortunately, the theoretical prediction of the C.T. band position is difficult because of the fact that the amine oxides are different in type from other n-donors or aromatic compounds, and that their ionization potentials as measured by the photoionization method have not been reported. Also, such a large red shift of the donor band caused by the iodine complex formation as is seen in Figures 7 and 8 is not known. It is, however, well known that the mechanism of hydrogen bonding and C.T. complex formation with iodine are similar from both the experimental and theoretical viewpoints^{25,35,38} and that the ultraviolet absorption band of these N-oxides shifts to shorter wave length when hydrogen bonding occurs.^{3d,5b,c,39} Also, when the HCl salt is formed, the absorption band of free pyridine N-oxide shown in Figure 7 shifts to 257 mμ (ε 2900).⁵ These facts show that the first of the above two interpretations is the more reasonable; that is, the longest wave length band may

(35) R. S. Mulliken, *J. chim. phys.*, **61**, 20 (1964).

(36) It is interesting to note that the interaction in benzene solvent between tribenzylamine N-oxide and bromophthalein magenta E (a dye having a phenolic OH group), studied by Davis and Hetzer,²⁶ shows that the basicity in terms of the association constant (l./mole) for the above system is 4.5-4.8 × 10⁵ and is larger than in the case of triethylamine under the same conditions (2.3 × 10⁴). These results also demonstrate the aliphatic amine N-oxide to be very strong electron donor.

(37) T. Kubota, *J. Pharm. Soc. Japan*, **75**, 1540 (1955), etc.; G. Pimentel and A. L. McClellan, "The Hydrogen Bond," W. H. Freeman and Co., Reinhold Publishing Corp., New York, N. Y., 1960, Appendixes B and C.

(38) (a) S. Nagakura, *J. chim. phys.*, **61**, 217 (1964); (b) S. Nagakura and M. Gouterman, *J. Chem. Phys.*, **26**, 881 (1957); (c) W. B. Person, *et al.*, *J. Am. Chem. Soc.*, **80**, 2049 (1958); **81**, 273 (1959); **82**, 29 (1960), etc.

(39) (a) M. Itoh and N. Hata, *Bull. Chem. Soc. Japan*, **28**, 260 (1955). (b) T. Kubota and M. Yamakawa, *ibid.*, **35**, 555 (1962), and other papers cited therein. (c) At the same time, the N-O stretching frequency undergoes a shift to lower frequency by the hydrogen bond formation (H. Sindo, *Chem. Pharm. Bull.*, **6**, 117 (1958); **4**, 460 (1956), etc.). This is a phenomenon similar to hydrogen bonding or iodine complex formation with a carbonyl group. That is, the C=O stretching frequency is shifted to a lower frequency by such molecular interactions (E. Augdahl and P. Klaeboe, *Acta Chem. Scand.*, **16**, 1637 (1962), etc.).

be considered the C.T. band. The blue shift of the original donor band caused by complex formation would now be explained as follows. In pyridine N-oxide and N-methylbenzaldoxime it has been shown that the highest filled molecular orbital has largely the nature of the original oxygen $2p\pi$ -orbital, since the orbital is considerably localized on the oxygen atom and the contribution of oxygen $2p\pi$ -orbital to other molecular orbitals is small.^{27, 28, 39b} The electronic transition corresponding to the band in question would have to cause electron migration from the oxygen atom to the rest of the π -electron system (pyridine ring for pyridine N-oxide) just as was discussed by Murrell⁴⁰ for aniline, etc., and a decrease in electron density at the oxygen atom will be expected in the excited state.^{39b} These effects will cause less stabilization of the complex in the excited state corresponding to the band of the donor itself than in the ground state, and thus result in a blue shift of the original donor band by iodine complex formation. In addition, the intensity of the original donor band is reduced. This phenomenon is similar to that which is observed with salt formation of pyridine N-oxide.⁵ The strong absorption bands appearing, respectively, at 318.4 and 342.5 $m\mu$ for pyridine N-oxide and N-methylbenzaldoxime may be now considered as C.T. bands, and the shifted iodine bands are clearly identified as those at 441 and 446 $m\mu$ for the former and the latter, respectively. The fact that the spectroscopic data tabulated in Table II are reasonable values in comparison with the corresponding data⁴ for other n-donors shows that the interpretation for the N-oxide-iodine complexes as being of $n-\sigma$ type³⁵ is very reasonable. The shortest wave length band for the complex observed only as an end absorption may be now considered the modified shorter wave length band of the donor itself.

Now, it is of interest to consider the possible configurations of the iodine complex of, for example, pyridine N-oxide. Let coordinate axes be taken as shown in Figure 11. $2px(\pi)$ -electrons will enter into conjugation with the ring π -electrons. Two extreme configurations may be considered: one in which the I_2 molecule lies in the xz plane as indicated by 1 in Figure 11, and another shown by 2, where the iodine lies in the yz plane. Intermediate configurations between the said two extreme cases also seem possible. It is noted that case 1 corresponds to case of a hybrid of an oxygen $2Px$ (i.e., $2p\pi$), $2s$, and $2pz$ orbitals as donor orbital, and case 2 to a hybrid of $2Py$, $2s$, and $2Pz$. An intermediate case would correspond to a hybrid of $2Px$, $2Py$, $2Pz$, and $2s$ as donor orbital. In Figure 11, the oxygen atom may be thought of approximately as having three "lone pairs," $2Px^2$, $(2s-2Pz \text{ hybrid})^2$, and $2Py^2$, but actually none of these are quite purely lone³⁵; for example, $2Px$ is somewhat mixed with ring π -orbitals by conjugation.

At the present time there is some difficulty in predicting the exact geometrical configuration. However, it should be noted that the X-ray analysis³⁶ of the pyridine N-oxide HCl salt (H-bonding complex) shows that the Cl atom does not lie in the yz plane but lies in an intermediate position which is closer to case 1 than to case 2 of Figure 11. The situation for the iodine complex of N-methylbenzaldoxime seems to be

(40) J. N. Murrell, *Proc. Phys. Soc.*, A68, 969 (1955).

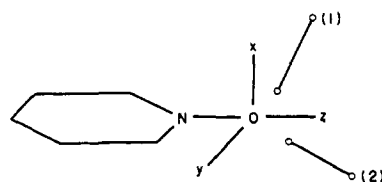


Figure 11. Models of the pyridine N-oxide-iodine complex (see text).

similar to that for the pyridine N-oxide-iodine complex, since the spectral behavior of the C.T. band of the former is analogous to that of the latter. However, the nature of the former complex is somewhat complicated, since N-methylbenzaldoxime may be distorted from the plane configuration, although the degree of the distortion seems to be small according to various experimental results.^{3d}

Next, we will consider the ultraviolet spectra observed for the I_2 complexes with trimethylamine and tribenzylamine N-oxides. For this case also the discussion of the wave length of the C.T. spectra is difficult for the reasons stated before for pyridine N-oxide, etc. However, it is found that the absorption band of trimethylamine N-oxide appearing at $\sim 202 m\mu$ with $\epsilon \sim 2350$ in acetonitrile solvent⁴¹ decreases strongly in intensity and undergoes a large blue shift in alcohol or aqueous solvents owing mainly to the hydrogen-bonding effect.²⁶ Keeping this fact and the close analogy⁴² between hydrogen bonding and iodine complexes in mind, the absorption spectra of the N-oxides in the complexes would be expected to shift to shorter wave length on complex formation. So, we can now safely assign the strong absorption bands, observed at 257 and 268 $m\mu$ for trimethylamine N-oxide and tribenzylamine N-oxide systems, respectively, to the C.T. absorption bands. Comparing the spectral data on the above-mentioned C.T. bands and shifted iodine bands listed in Table II (ϵ , f , $\Delta\nu_{1/2}$, etc.) with those of pyridine N-oxide-iodine and N-methylbenzaldoxime-iodine complexes, we can note that each value of the former is much larger than that of the latter. These results are compatible with those derived from the larger K and ΔH values for the former than those of the latter, and suggest that the former are stronger $n-\sigma$ complexes than the latter. Here again it is difficult to answer the question as to the expected geometrical configurations of the complexes. On this question no direct information is available. However, the X-ray analysis of the trimethylamine N-oxide HCl salt, where a strong hydrogen bond like $O \cdots H \cdots Cl$ is considered, shows that the HCl molecule combines with the oxygen atom in the amine oxide and lies in the same σ_v -plane as that occupied by a $O-N-C_1$ bond.⁴³ The angle of $Cl-O-N$ is 110.4° to the opposite

(41) This seems to be due to the $N \rightarrow Q$ transition from the viewpoint of the spectral behavior written here. The spectrum in dichloromethane seems to be almost the same as in acetonitrile, although the spectrum in the wave-length region less than 213 $m\mu$ could not be recorded because of the high absorption of solvent (0.01-cm. cell). In addition, thanks are due to Mr. M. Yamakawa in Shionogi Research Laboratory, who also measured the ultraviolet spectra of trimethylamine N-oxide in CH_3CN by means of the Beckman far-ultraviolet spectrophotometer using thin cells.

(42) This analogy was also recently stressed by O. Hassel, Abstracts, 146th National Meeting of the American Chemical Society, Jan. 23, 1964, at Denver, Colo., p. 32D.

(43) $(CH_3)_3NO$ is almost in C_{3v} symmetry.

side of the N-C₁ bond. Supposing that the present iodine complex has a similar configuration, it seems reasonable that the electron-donor orbital of the oxygen is a hybrid of 2p with some 2s, just as for the dioxane-halogen complex as discussed by Mulliken.³⁵

Acknowledgments. The author wishes to express his sincere thanks to Professor R. S. Mulliken for giving

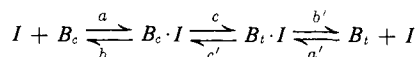
him the opportunity to work at the University of Chicago and for his interest, various suggestions, and reading of the manuscript. He also wishes to thank Dr. M. L. Ginter and other members of the spectroscopic laboratory for helpful advice in the experimental work and for their hospitality. Financial support from the National Science Foundation is gratefully acknowledged.

Iodine-Catalyzed Isomerization of Olefins. III. Kinetics of the Geometrical Isomerization of Butene-2 and the Rate of Rotation About a Single Bond

Sidney W. Benson, Kurt W. Egger, and David M. Golden

Contribution from the Stanford Research Institute, Menlo Park, California.
Received August 28, 1964

The kinetics of the gas phase, I₂-catalyzed geometric isomerizations of *cis*- or *trans*-butene-2 (B_c, B_t) have been studied over the temperature range 410 to 520°K. The rate law has the form $-d(B_c)dt = k(B_c)(I_2)^{1/2} [1 - (B_t)/K_{eq}(B_c)]$ which is shown to be consistent with the consecutive-step mechanism involving I atom addition to the π-bond.



From an analysis of the steady-state rate for this system and reasonably good estimates of the various rate constants in the scheme, it is shown that the rate-determining slow step in the system is *c* (or *c'*), the rotation about a single bond in the radicals B_c·I (or B_t·I). From the observed rate constant *k*_{obsd} and an estimate of the equilibrium constant K_{a,b} it is found that the rotational rate constant *k*_c equals 10^{11.2} × 10^{-3.3/θ} sec.⁻¹ (where θ = 2.303RT in kcal./mole). This compares well with the value estimated from transition state theory and bond energies, *k*_{c(est.)} = 10^{11.3} × 10^{-3.5/θ} sec.⁻¹. These appear to be the maximum rate constants ever measured for a chemical change. By thermodynamic and kinetic analysis of the data on other *cis-trans* isomerizations, both catalyzed and uncatalyzed, it is shown that a similar mechanism may be used to estimate the rates. From the data on the NO-catalyzed isomerizations it may be deduced that the C-N bond dissociation energy in alkyl nitroso compounds is about 37 kcal. Rate constants in gas phase and solution appear to be very similar.

Introduction

I₂ has long been recognized as one of the extremely effective catalysts for the *cis-trans* isomerization of olefins. Where rate studies have been made, the rate law generally follows the form, rate ∝ (I₂)^{1/2}(olefin).

The appearance of the half-order dependence on I₂ has been interpreted as involving an I atom addition to the olefin as part of the mechanism. If this radical mechanism is correct, then the rate-determining step could be either the rate of internal rotation of the two

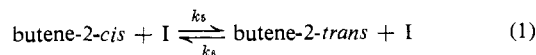
groups in the radical or else the actual addition of the I atom to the olefin. The former possibility is a rather interesting one since it would provide for the first time the prospect of observing the rate of rotation around a single bond as the rate-determining step in a chemical reaction. In the present paper we shall report our kinetic studies of the I₂-catalyzed isomerizations of butene-2 in the gas phase in which we find that the rate-determining step is indeed the rate of rotation about a single bond. In the final sections we shall also discuss a number of related studies by other authors on *cis-trans* isomerizations, both catalyzed and uncatalyzed, and show that they follow a similar radical pathway.

Experimental

Very briefly the study consisted of mixing I₂ vapor and *cis*- or *trans*-butene-2 vapor in the gas phase in a thermostated glass reaction vessel in the absence of light and then after predetermined periods of time quenching the entire reaction and analyzing the products. The method used was a variation of that employed by Benson, *et al.*,^{1,2} in their studies of the butene-1-butene-2 isomerization and has been reported on in detail earlier.^{3a,b} The *cis-trans* isomerization is the fastest reaction in the system and can be carried out at temperatures where the positional isomerization is negligibly slow.

Results

For the reaction



the rate expression is

$$-\frac{d(B_c)}{dt} = k_5(B_c)(I) \left(1 - \frac{(B_t)}{K_{5,6}(B_c)} \right) \quad (2)$$

(1) S. W. Benson and A. N. Bose, *J. Am. Chem. Soc.*, **85**, 1385 (1963).

(2) S. W. Benson, A. N. Bose, and P. S. Nangia, *ibid.*, **85**, 1388 (1963).

(3) (a) D. M. Golden, K. W. Egger, and S. W. Benson, *ibid.*, **86**, 5416 (1964), part I of this series; (b) *ibid.*, **86**, 5420 (1964), part II.