and isotope effect are expected for reaction 2. Reaction 3, however, may proceed through an excited intermediate as represented by

$$H_3O^+ + e \longrightarrow H_3O^* \longrightarrow H + H_2O \qquad (18)$$

Our observed low value for the isotope effect in the gas phase may imply simply that thermal equilibration of excited intermediates is less likely than that in the liquid medium.

Acknowledgment. We are indebted to Dr. M. Cher of our laboratory for valuable suggestions, and we wish to thank Mr. R. A. Meyer and Mr. F. Munich for mass spectrometric analyses and Mr. E. A. Eisel for the construction of irradiation cells.

Dipole Moments of Amine–Iodine "Complexes." A Question[1]

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Contribution from the Department of Chemistry, University of Iowa, Iowa City, Iowa. *Received November 4, 1965*

Abstract: Experimental measurements of the dipole moments of three amine–iodine "complexes" confirm the values previously reported for the pyridine–iodine complex (Kortum and Walz) and also for the triethylamine–iodine complex (Tsubomura and Nagakura). An analysis of the atomic and electronic polarization terms establishes that the order of magnitude of the error introduced when these terms are neglected in the usual treatment of data from complexes is about 10%, for either weak or strong complexes with I_2. The very large values for the experimental dipole moments of the trialkylamine–iodine complexes in dioxane solution, combined with the ultraviolet spectra, suggest very strongly that the predominant species in these solutions is an ion pair with I_3^- as the negative ion. Thus, the very important values of the dipole moments of these complexes remain in question.

From the theoretical point of view, one of the more interesting experimental properties of electron donor–acceptor complexes is the dipole moment. As Mulliken[3] noted, the dipole moment of the complex can be directly related to the coefficient, *b*, measuring the contribution of the dative structure to the structure of the complex

$$\psi_N = a\psi_0 + b\psi_1 \qquad (1)$$

Here ψ_N is the wave function for the complex in its ground state. Its approximate form is given in terms of two hypothetical idealized structures, the "no-bond" state (D. . . A) with wave function ψ_0, and the "dative" state ($D^+–A^-$), with wave function ψ_1. The coefficients *a* and *b* measure the importance of each of these hypothetical states.

According to Mulliken,[3] for a weak complex between nonpolar molecules, the dipole moment of the complex is given approximately by

$$\mu \simeq b^2\mu_1 \qquad (2)$$

The value of μ_1, the dipole moment of the dative structure, can be estimated from a knowledge of the geometry of the complex; in general, it will be quite large because of the high charge separation in the dative structure. Hence, a measurement of the dipole moment of the complex can give a direct measure of the coefficient *b*. The application of these ideas has been illustrated by Briegleb[4] for some complexes.

A careful examination of the dipole moment data reviewed by Briegleb[4] reveals that agreement on the experimental values found by different workers is not always perfect. Further consideration suggests that one should observe caution in this interpretation of the data, since one must remember that the electronic and atomic polarization of the complex might change significantly from that of the components, thus leading to an apparent dipole. This subject has been discussed by Anderson and Smyth,[5] who have illustrated the power of the technique of measuring dielectric constants over a wide range of frequencies as applied to these complexes. They have shown that the benzene–iodine and dioxane–iodine complexes dissociate at a rate comparable to the rate of relaxation of the polar complex in solution, thus complicating the results.

In our studies we were concerned with some relatively strong amine complexes of I_2 with the goal of obtaining *b* values so that these may be used to correlate with other properties of these complexes, particularly the infrared spectrum.[6] Because of the known lack of reproducibility in the literature of dipole moments of complexes, and because of the general reactivity of I_2 with amines and with metal cells, etc., it seemed desirable to repeat measurements already given for pyridine–iodine[7,8] and for triethylamine–iodine.[9] Since the most complete far-infrared study on I_2 complexes is that by Yada, Tanaka, and Nagakura[10] on the tri-

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[2] On leave of absence from Department of Chemistry, Kumamoto University, Kumamoto, Japan, 1963–1964. Reprint requests should be directed to Dr. Person.

[3] R. S. Mulliken, *J. Am. Chem. Soc.*, **74**, 811 (1952).

[4] G. Briegleb, "Elektronen-Donator-Acceptor Komplexe," Springer-Verlag, Berlin, 1961.

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[6] (a) H. B. Friedrich, Ph.D. Thesis, University of Iowa, 1963; (b) H. B. Friedrich and W. B. Person, *J. Chem. Phys.*, to be published.

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[8] Y. K. Syrkin and K. M. Anisimova, *Dokl. Akad. Nauk SSSR*, **59**, 1457 (1948).

[9] H. Tsubomura and S. Nagakura, *J. Chem. Phys.*, **27**, 819 (1957).

[10] H. Yada, J. Tanaka, and S. Nagakura, *J. Mol. Spectry.*, **9**, 461 (1962).

methylamine–iodine complex, we wanted especially to include that complex in our study.

Instead of the simple, direct, experimental result that we had expected and desired, we found that our measurements are inconsistent with the idea that amine–iodine *complexes* exist in solution in dioxane. We believe our measurements must be interpretated as evidence for ion pairs, such as $(Et_3NH)^+\cdots I_3^-$, or $Et_4N^+\cdots I_3^-$, in these solutions.

Experimental Section

A Kahlsico Dipolmeter Type DM-01 was used with the Type DFL-1 gold-plated metal cell in measuring the dielectric constants. This instrument operates at a frequency of approximately 2.0 Mc, with a measuring sensitivity of $\Delta\epsilon/\epsilon = 4 \times 10^{-5}$. The temperature of the measuring cell was kept constant by circulating water from a bath controlled at 25 ± 0.03°. The cell constant was obtained by calibrating[11] with benzene (ϵ 2.2727)[12] and with cyclohexane (ϵ 2.0148).[13]

The specific volumes were obtained by the method given by Lipkin, *et al.*,[14] using 3- or 5-ml pycnometers.

Solutions were made by weight, including the I_2 and the $(CH_3)_3N$ solutions. All weighings were made on a Mettler semimicrobalance. *n*-Heptane was used as a solvent for the pyridine–I_2 complex, and *p*-dioxane was used as a solvent for the trimethyl- and triethylamine complexes. Most of the measurements were made in solutions prepared by weighing the I_2 into a volumetric flask, then adding solvent to form a stock solution. Varying amounts of donor (by weight) were added to different portions of the I_2 solution to form the solutions of the complex.

The dielectric constant of the solution was measured on the Dipolmeter; the density of this same solution was determined using the pycnometer. Several solutions could be treated each day. The dielectric constant of the solvent was determined each day as a check that the cell constant was the same. In order to minimize the effect of H_2O on our results, an attempt was made to remove it from the glassware used in the measurements by flushing with dry N_2.

Solvents were purified according to standard procedures.[15]

From the measured dielectric constant of the solution, the polarization of the complex was calculated from the measured polarization of the solution, P_{soln}, according to eq 5 of the Discussion (see ref 7). The concentration of complex was computed from the known concentrations of the components and the formation constants for the complexes (K_c = 100 for $Py\cdot I_2$;[16,17] K_c = 6300 for $Et_3N\cdot I_2$;[18] K_c = 12,100 for $Me_3N\cdot I_2$.[19] The resulting values for the polarization of the complex vary somewhat as a function of concentration, presumably owing to interactions between neighboring ion pairs. Typical plots are given in Figure 1. The polarization at infinite dilution, $P_{\infty 2}$, is then used to compute the dipole moments for the complex

$$\mu = 0.0128\sqrt{(P_{\infty 2} - P'')T} \tag{3}$$

Here P'' is the polarization of the separated component molecules of the complex, and T is the absolute temperature.

Results

The results are summarized graphically in Figure 1. From the extrapolation of the data according to the straight lines given there, we find the dipole moments for the complexes given in Table I. We see there that our values for the dipole moments of the complexes verify those already reported. Our value for the pyridine complex showed the greatest scatter owing to the difficulty in measuring accurately the moment of this weak complex. Furthermore, the larger dipole moment of pyridine made it somewhat more difficult to correct properly for the polarization of the uncomplexed pyridine. Our value for the dipole moment of the triethylamine–iodine complex is somewhat larger than that given by Tsubomura and Nagakura[9] because of the concentration dependence of $P_{\infty 2}$ as shown in Figure 1. As we see there, the values of P_2 which they reported are in reasonable agreement with our values in that concentration range. The essential result of their work, the very large dipole moment, remains unchanged.

Table I. Dipole Moments for Some Amine–Iodine Complexes

Solute	$P_{\infty 2}$	μ,[e] D.	μ_{lit}, D.
$Py\cdot I_2$[a]	500 ± 50	4.90 ± 0.30	4.5[c]
$Et_3N\cdot I_2$[b]	3230 ± 45	12.44 ± 0.10	11.3[d]
$Me_3N\cdot I_2$[b]	2120 ± 41	10.05 ± 0.1	
Py	129.1000[c]		2.28[e]
I_2	31.1000[c]		0
Et_3N[b]	47.2000[d]		
Me_3N[b]	33.3000[e]		
n-Heptane	34.4650[f]	0	
p-Dioxane	24.6702[f]		0.21[c]

[a] In *n*-heptane solution. [b] In *p*-dioxane solution. [c] Reference 7. [d] Reference 9. [e] Measured; this work. [f] Measured on pure solvent for each set of solutions. The deviation of these values from literature values represent the scatter due to changing cell constant. The value given here is a typical measured value for one set of runs.

Discussion

Since our results for the dipole moment of the pyridine–iodine complex are in agreement with the literature values,[7,8] we regard that value as established and our conclusions about the magnitude are in essential agreement with those given elsewhere.[4] Hence, we shall not discuss further our results for this complex.

Before examining in detail the questions raised by the magnitude of μ for the aliphatic amine–iodine complexes, let us first consider the importance of the changes in atomic and electronic polarization of the complex compared to the pure components in interpreting the measured dipole moment of the complex. We shall not expect these changed polarizations to influence the interpretation of the results for strong complexes significantly, but we should consider their importance for the case of weak complexes.

The complex differs from the separated components in that it has some new spectral properties: in particular, a new strong electronic absorption band (the charge-transfer band) at longer wavelength (usually) than the strong electronic absorption bands of the separated components. Furthermore, there are some new absorption bands in the far-infrared spectrum of the complex associated with the vibrations of the entire donor molecule against the acceptor, and with the induced absorption of the I_2 stretching vibration. By estimating frequencies and intensities of these new absorption bands, we can compute their contribution to the polarization of the complex. If all other absorptions are not greatly different in the complex from those in the separate components, then we may assume that

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(11) Kahlsico Instruction Manual.

(12) R. Mecke and K. Rosswog, *Z. Elektrochem.*, **60**, 47 (1956).

(13) K. Rosswog, Dissertation, Freiburg, 1953.

(14) M. R. Lipkin, *et al.*, *Ind. Eng. Chem. Anal. Ed.*, **16**, 55 (1944.)

(15) A. Weissberger, *et al.*, "Techniques of Organic Chemistry," Vol. 7, "Organic Solvents," 2nd ed, Interscience Publishers Inc., New York, N. Y., 1955.

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(17) A. I. Popov and R. H. Rygg, *J. Am. Chem. Soc.*, **79**, 4622 (1957). Professor Popov informs us that K_c should be somewhat larger than 100; this correction will not materially affect our results.

(18) S. Nagakura, *ibid.*, **80**, 520 (1958). The solvent was *n*-heptane.

(19) H. Yada, J. Tanaka, and S. Nagakura, *Bull. Chem. Soc. Japan*, **33**, 1660 (1960) (in *n*-heptane).

these new absorption bands will be the only cause for a changed polarization of the complex as compared to its components. In an attempt to determine quantitatively the change in the atomic and electronic polarization of the complex compared to the components, so that the corrected orientation polarization for the complex can be computed, we have made the following analysis.

In the absence of interaction, the total polarization of a solution of a donor, D, and acceptor, A, is

$$P_{\mathrm{soln}}^0 = X_0P_0 + X_{\mathrm{A}}^0P_{\mathrm{A}} + X_{\mathrm{D}}^0P_{\mathrm{D}} \qquad (4)$$

Here X_0 is the mole fraction of the solvent, X_{A}^0 is the mole fraction of the acceptor, P_0 is the polarization of the solvent, etc. If there is interaction, then $n_{\mathrm{T}}X_{\mathrm{DA}}$ moles of complex form with polarization, P_{DA}, and $n_{\mathrm{T}}X_{\mathrm{DA}}$ moles of donor and acceptor are used up. Hence, the polarization of the solution after interaction is

$$P_{\mathrm{soln}} = X_0P_0 + (X_{\mathrm{D}}^0 - X_{\mathrm{DA}})P_{\mathrm{D}} + (X_{\mathrm{A}}^0 - X_{\mathrm{DA}})P_{\mathrm{A}} + X_{\mathrm{DA}}P_{\mathrm{DA}} \qquad (5)$$

Hence the change in polarization due to the interaction is

$$\Delta P = P_{\mathrm{soln}} - P_{\mathrm{soln}}^0 = -X_{\mathrm{DA}}(P_{\mathrm{A}} + P_{\mathrm{D}}) + X_{\mathrm{DA}}P_{\mathrm{DA}} \qquad (6)$$

Now, the polarization is to be interpreted as

$$P_i = P_i^{\mathrm{el}} + P_i^{\mathrm{at}} + P_i^{\mathrm{or}} \qquad (7)$$

Here P_i^{el} is the electronic polarization, P_i^{at} is the atomic polarization, and P_i^{or} is the orientation polarization term. The dipole moment is computed from the latter term, using eq 3 (with $P_{\infty 2} - P'' = P_{\mathrm{DA}}^{\mathrm{or}}$). For nonpolar donor and acceptor molecules (and perhaps also for polar molecules) we may assume that the atomic and electronic polarization of the complex is the sum of the polarizations of the component molecules, except for an additional term due to the interaction; *i.e.*

$$P_{\mathrm{DA}}^{\mathrm{el}} \simeq P_{\mathrm{D}}^{\mathrm{el}} + P_{\mathrm{A}}^{\mathrm{el}} + P_{\mathrm{CT}}^{\mathrm{e}}$$

$$P_{\mathrm{DA}}^{\mathrm{at}} \simeq P_{\mathrm{D}}^{\mathrm{at}} + P_{\mathrm{A}}^{\mathrm{at}} + \sum_{i=1}^{6} P_i^{\mathrm{at}}$$

Here we have assumed that the electronic interaction term arises solely from the new charge-transfer band, and that the change in atomic polarization arises from the five new vibrational bands due to the vibrations of the donor against the (diatomic) acceptor, plus the enhanced band of the acceptor. This is only approximately correct, because the vibrational spectrum of the donor changes in other vibrations, as does the electronic spectrum. However, with these assumptions

$$\Delta P = X_{\mathrm{DA}}(P_{\mathrm{CT}}^{\mathrm{el}} + \sum_{i=1}^{6} P_i^{\mathrm{at}} + P_{\mathrm{DA}}^{\mathrm{or}})$$

Thus, we need to estimate the magnitudes of $P_{\mathrm{CT}}^{\mathrm{el}}$ and $\sum_{i=1}^{6} P_i^{\mathrm{at}}$ and compare them with $P_{\mathrm{DA}}^{\mathrm{or}}$ in order to determine the error in neglecting them and attributing the entire change in polarization to $P_{\mathrm{DA}}^{\mathrm{or}}$, as is usually done.

The magnitude of the polarization terms can be estimated from the known spectroscopic properties of the complex. Thus[20]

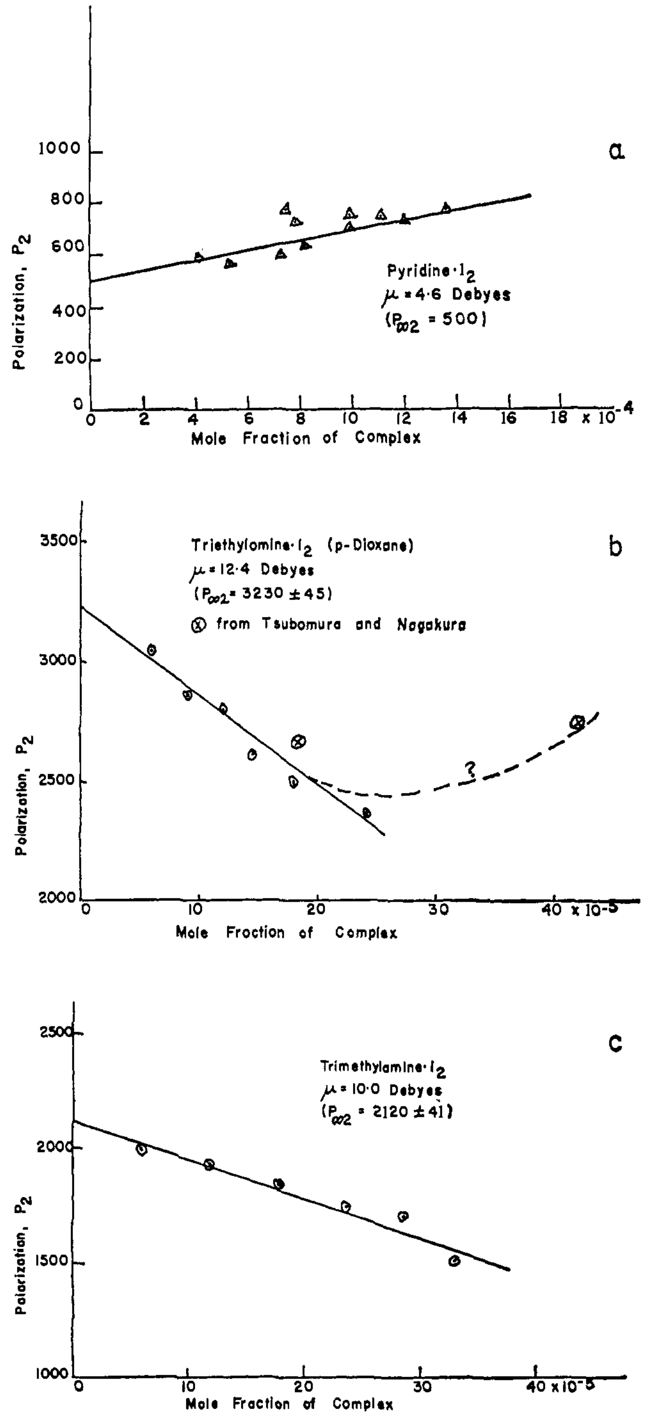

Figure 1. Polarization of the amine–iodine complexes as a function of concentration: (a) pyridine–iodine, (b) triethylamine–iodine, (c) trimethylamine–iodine.

$$P_{\mathrm{CT}}^{\mathrm{el}} = 1.80 \times 10^{10} f_{\mathrm{CT}}/\omega^{2\mathrm{CT}}$$

and

$$P_i^{\mathrm{at}} = (1/3\pi^2)(\Gamma_i/\omega_i)$$

Here, f_{CT} is the oscillator strength for the charge-transfer band at wavenumber ω_{CT}; Γ_i is the intensity, as defined by Crawford,[21] for the infrared absorption band at wavenumber ω_i.

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(20) Derived from relations given by D. H. Whiffen, *Trans. Faraday Soc.*, **54**, 327 (1958).

(21) B. Crawford, Jr., *J. Chem. Phys.*, **29**, 1042 (1958).

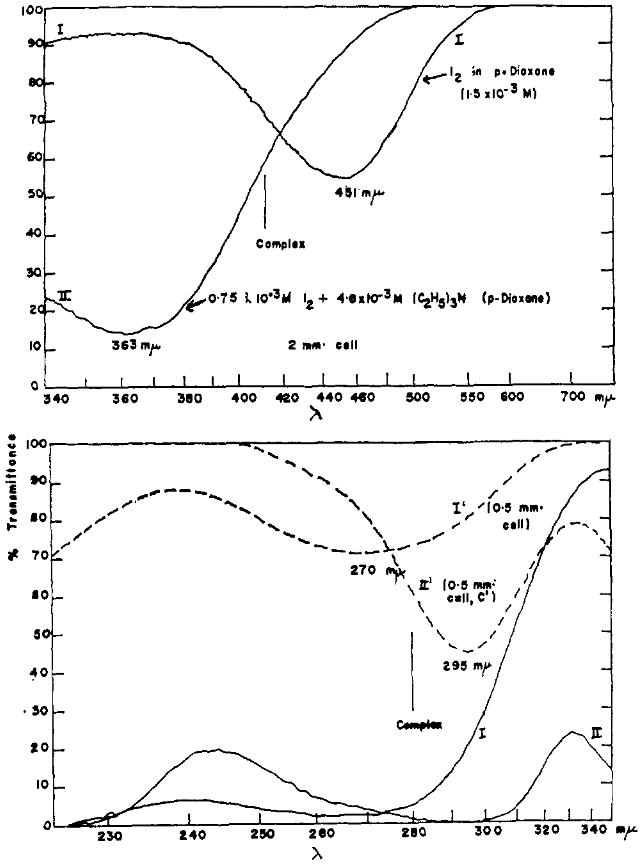

Figure 2. Ultraviolet and visible spectra of (I) iodine in dioxane; (II) iodine and triethylamine in dioxane (———, 2-mm cell; ---------, 0.5-mm cell).

The parameters used, and the value of P_{CT}^{el}, are given in Table II for a few typical complexes. We see there that even for the case of the very weak benzene–iodine complex, P_{CT}^{el} is, at most, only about 10% of the observed change in polarization. Hence, complete neglect of this quantity, as in the usual treatment, introduces a reasonably small error, especially when compared to the usual experimental error in μ.

Table II. Estimation of the Electronic Polarization, P_{CT}^{el}, for Some Complexes with I_2

Donor	ω_{CT}, cm^{-1}	f_{CT}	P_{CT}^{el}	ΔP_{obsd}
Benzene	34,000[a]	0.38[a]	5.9	67[b]
Pyridine	42,600[c]	1.1[c]	10.9	500[d]
Trimethylamine	38,000[e]	1.1[f]	13.8	2120[d]

[a] Taken from or estimated from values given in ref 4. [b] Reference 7. [c] H. Tsubomura and R. P. Lang, *J. Am. Chem. Soc.*, **83**, 2085 (1961). [d] This work. [e] Reference 19. [f] S. Nagakura, private communication.

Similarly, Table III gives the data and calculation of $\sum_{i=1}^{6} P_i^{at}$ for the strong trimethylamine–iodine complex, where the effect should be the largest. The intensities (Γ) are all estimated values which are probably too high, in order to be sure that the estimated values of P_i^{at} are large enough. Thus, it seems very unlikely that neglect of the changed atomic polarization on complexing can contribute significantly to an error in interpreting the change in polarization as coming entirely from P_{DA}^{or}.

Table III. Estimation of the Atomic Polarization Due to the New Absorption Bands in the Trimethylamine–Iodine Complex

Mode	ω,[a] cm^{-1}	Γ,[b] cm^2/mole	P_i^{at}
I–I	185	9,000	1.6
N–I	145	11,500	2.7
δ_1(N–I–I)	100(2)	2,000	1.3
δ_2(N–I–I)	50(2)	4,000	1.3
			ΣP_i^{at} = 6.9

[a] The frequencies of the I–I and N–I stretching motions are from ref 10; the other values are "educated guesses." [b] The intensities are "educated guesses," and are meant to be upper limits of the reasonable estimates which could be made.

Having established the small magnitude of the error due to neglecting the changes in electronic and atomic polarization upon complexing, it seemed that we might now proceed to interpret our measured dipole moments (Table I) in terms of the dative coefficients, *b*. However, before proceeding to do so, we should note, with some alarm, the magnitudes of the experimental dipole moments. We note especially the very large change in μ from the pyridine–iodine to the trimethylamine–iodine complex, even though there is little shift in other properties, such as the infrared spectrum of the complexed I_2, for example. Kosower has noted that these very high values of μ suggest ion pairs rather than complexes.[22]

The similarity between the dipole moments reported in Table I for the I_2 complexes with trimethyl- and with triethylamine and the dipole moments for ion pairs is illustrated in Table IV. The close comparison in values listed there is very suggestive indeed. Attempts to estimate the dipole moment for an ion such as $(R_3NH)^+\cdots I_3^-$ suggest that the dipole moment should be about 12–15 D., without correcting for the decrease due to the polarization. Hence, it seems quite likely that our observations for the alkylamine–iodine "complexes" are rather for the ion pairs.

Table IV. Comparison of the Measured Dipole Moments of Amine–Iodine "Complexes" with Those for Known Ion Pairs (Ammonium Picrate (Pi) Salts)[a]

Species	Solvent	ΔP_{obsd}	μ_{app}, D.
$Me_3N \cdot I_2$	Dioxane	2120	10.0
$Et_3N \cdot I_2$	Dioxane	3230	12.4
$(Et_3NH)^+Pi^-$	Benzene	2850	11.7
$(n\text{-}Bu_3NH)^+Pi^-$	Benzene	2940	11.9
$(n\text{-}Bu_3NH)^+Pi^-$	Dioxane	3090	12.2

[a] The values for the ammonium picrate salts are from A. A. Maryott, *J. Res. Natl. Bur. Std.*, **41**, 1 (1948).

In order to test these ideas, we examined the ultraviolet spectrum of solutions of triethylamine and I_2 in dioxane, under approximately the same conditions as for the dipole moment studies in order to determine the species existing in solution.

Solutions of triethylamine and I_2 were prepared in dioxane of similar concentrations to those used for the dipole moment measurements. Spectra were obtained

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(22) E. Kosower, *Progr. Phys. Org. Chem.*, in press.

on a Hitachi EPS-2U spectrometer, using 2-mm and 0.5-mm quartz cells. A typical spectrum is given in Figure 2. We see there that the spectrum of the "complex" shows no absorption peak at 280 mμ, as is observed characteristic of the complex in *n*-heptane solutions;[18] instead we see the double peak (absorption maxima at 363 and 295 mμ) characteristic of the spectrum of I_3^-.[23] In fact, it seems quite obvious from Figure 2 that the "complex" in dioxane solution has all the iodine present as I_3^-, with practically none present as I_2 complex.[24]

We conclude, therefore, that our studies of the dipole moments of alkylamine complexes of I_2 in dioxane, together with the study of the spectrum, indicate that the predominant species in this solution is the ion pair, not the complex. This possibility has been recognized earlier;[9,22] our studies simply verify it. We do not question the existence of the trialkylamine–iodine complexes in *n*-heptane solution, but in the slightly more polar dioxane solution it is certainly not the dominant species. (It is possible that traces of water cause some reaction to form the ion pairs.) Thus, the theoretically important value of μ for these complexes remains elusive. It is our opinion that this quantity will be quite hard to obtain accurately, since the complexes do not have sufficient solubility in nonpolar solvents such as *n*-heptane, and the ion-pair formation in slightly polar solvents will complicate any studies there. Our question, then, is: "What is the dipole moment for trialkylamine–iodine complexes?"[25]

Acknowledgments. Financial support from the Army Research Office (Durham) and from Public Health Service Research Grant No. GM-10168 is gratefully acknowledged. It is a pleasure to acknowledge the helpful correspondence with Professors S. Nagakura and E. M. Kosower, and the cooperation of Dr. H. D. Bist with the spectroscopic studies to verify those reported here.

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[23] A. I. Popov and R. F. Swensen, *J. Am. Chem. Soc.*, 77, 3724 (1955).

[24] This conclusion has been reinforced strongly by a much more complete spectroscopic study of the nature of the species present in solutions of triethylamine and I_2 in dioxane, carried out in this laboratory by Dr. H. D. Bist (to be published). The positive ion has not been established with certainty, but Et_3NH^+ or Et_4N^+ seem possible. It would be desirable, certainly, to attempt to repeat these measurements under more rigorously anhydrous conditions in order to determine which ion is present. However, we have made here normally rigorous attempts to reach these anhydrous conditions.

[25] Professor S. Nagakura has informed us in a private communication that he has answered this question for complexes of I_2 with mono- and dialkylamines (but not for trialkylamines) by a carefully conducted study, which will be published shortly; *e.g.*, he finds for diethylamine–iodine, μ = 7.0 (in dioxane) or 6.2 D. (in benzene). For isopropylamine–iodine, μ = 7.4 (in dioxane) and 6.2 D. (in benzene).

The Kinetics of Hydrolysis of the Dinitrobis(ethylenediamine)cobalt(III) Ion in Various Concentrated Acid Solutions

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Contribution from the Department of Chemistry, Virginia Polytechnic Institute, Blacksburg, Virginia.

Received August 2, 1965

Abstract: Hydrolysis rates of *trans*-$[Co(en)_2(NO_2)_2]^+$ were obtained as a function of acid concentration in perchloric, hydrochloric, hydrobromic, sulfuric, and nitric acids at 25°. Values of the parameters in Bunnett's equations are consistent with attack of water on the protonated complex as the rate-determining step. In all acids except perchloric the rate-determining reaction is followed by anation of the nitroaquo intermediate. Arrhenius plots for perchloric acid were linear, with an activation energy of 23.6 ± 0.8 kcal and an activation entropy of 2.9 ± 2.3 eu at the 95% confidence level. For the other acids, curvature increasing with acid concentration and temperature was noted in the Arrhenius plots. This behavior is consistent with two consecutive reactions, the second having the lower activation energy.

Interest in the reactivity of coordination compounds has been so great that several reviews have been written[3] since the classic monograph on the subject.[4] In the hydrolysis reaction, $[Co(en)_2(X)(Y)]^+ + H_2O \rightarrow [Co(en)_2(X)(H_2O)]^{2+} + Y^-$, the nature of the orienting ligand "X" in determining the mechanism of reaction has been emphasized.[3e] Electron-withdrawing groups such as nitrite assist reaction by an S_N2 path, while electron-releasing groups promote S_N1 reactions. At the time this investigation was begun, little information was available on the role of the replaced ligand "Y" except when Y is a halide. Study of the hydrolysis of the dinitro compounds was initiated to show the effect of Y on the rate and to attempt to formulate a mechanism for the hydrolysis.

Since these dinitro complexes are very unreactive, study of the hydrolysis reaction at high acid concen-

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[1] Based on a dissertation by D. Lambert in partial fulfillment of the requirements for the degree of Doctor of Philosophy at Virginia Polytechnic Institute, 1965.

[2] To whom requests for reprints should be addressed.

[3] (a) F. Basolo in "Survey of Progress in Chemistry," Vol. 2, A. F. Scott, Ed., Academic Press Inc., New York, N. Y., 1964, p 1; (b) F. Basolo and R. G. Pearson, *Advan. Inorg. Chem. Radiochem.*, 3, 1 (1961); (c) C. K. Ingold, "Substitution at Elements Other Than Carbon," Weizmann Science Press, Jerusalem, 1959, Chapter 1; (d) D. R. Stranks, in "Modern Coordination Chemistry," J. Lewis and R. G. Wilkins, Ed., Interscience Publishers Inc., New York, N. Y., 1960, p 78; (e) M. L. Tobe, *Sci. Progr.*, **48**, 483 (1960); (f) R. G. Wilkins, *Quart. Rev.* (London), **16**, 316 (1962).

[4] F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1958.