instances where comparative data are available on the reactivity of free and coördinated aromatic ligands are collected in Table IV. With the exception of tropolone, there are no authenticated instances where coördination changes the reactive position of an aromatic ligand toward electrophilic reagents.

One final important factor must be mentioned. This is the effect of charge on reactivity that arises when a neutral ligand coördinates to a metal ion to produce a charged complex. This effect of charge may be expected to be rather considerable but may also be masked by ion - pair formation which is often extensive with large, highly charged ions.[15]

The introduction of a highly charged cation in the neighborhood of a neutral ligand such as would result from complexing is known to result in an appreciable deactivation of the ligand towards certain reagents which probably attack the ligand "positive-end on."[16]

Spectrophotometric Evaluation of the Thermodynamic Data for the Formation of the Dimethylbenzamide–Iodine Addition Compound

By Robert L. Carlson[1] and Russell S. Drago

The free energy and enthalpy of association of the addition compound formed between dimethylbenzamide and iodine are reported. Values of $-\Delta H = 4.0 \pm 0.2$ kcal./mole and $K = 3.8 \pm 0.1$ l. mole^{-1} at 25° are obtained. Changes in the molar absorptivity of iodine and the complex are observed with changes in temperature in some spectral regions. These changes can lead to an appreciable, systematic error in the enthalpy calculation if neglected. A procedure is indicated for obtaining reliable data on systems where these changes are occurring. Comparison of the heat of formation of the iodine adduct of N,N-dimethylbenzamide with values reported for a series of aliphatic amides and with the σ^* values for these amides indicates that the benzene ring is conjugated with the amide group.

Introduction

In a recent publication[2] a procedure referred to as an enthalpy determination was reported for evaluating heats of formation of weak molecular complexes. In this procedure the differences in absorbance between an iodine solution and a single iodine-base solution are measured as a function of temperature. The equilibrium constant K and molar absorptivity of the complex ϵ_C are determined at 25° by the standard methods.[3,4] The molar absorptivity obtained at 25° is employed for all temperatures, and K at different temperatures is calculated from the absorbance readings. Excellent reproducibility in the ΔH values (to ± 0.1 kcal.) is obtained at a given wave length. The calculated heat varies only slightly when $\epsilon_C - \epsilon_I$ is varied within the limits of error of its determination as long as it is constant at all temperatures. The calculated equilibrium constant varies considerably with changes in the value of $\epsilon_C - \epsilon_I$ at a given temperature, depending strongly upon the magnitude of K and the concentrations of the reactants. As a result, a slight change in either or both ϵ_C or ϵ_I with temperature will result in an appreciable difference in the actual value for ΔH and the one calculated assuming constant $\epsilon_C - \epsilon_I$.[5]

It is found that at different wave lengths, different values are obtained for ΔH. It is proposed[2] that ϵ_C and ϵ_I change with temperature and both the magnitude and direction of the change is wave length dependent. This proposal is borne out in this article by a careful analysis of the absorption spectra obtained for solutions containing N,N-dimethylbenzamide and iodine.

It should be emphasized that the errors introduced by a changing value of $\epsilon_C - \epsilon_I$ with temperature do not invalidate the use of this procedure for determining ΔH. In the classical procedure,[3,4] errors in the preparation of the individual solutions result in errors in the calculated values of $\epsilon_C - \epsilon_I$ and ΔH which are greater than the errors we discuss. This is verified by the random values reported in the literature for changes of $\epsilon_C - \epsilon_I$ with temperature. Errors of the order of magnitude being discussed (± 0.7 kcal./mole at 95% confidence) are normally encountered in the evaluation of ΔH by the classical procedures at certain wave lengths. A procedure is described for carrying out these measurements with a precision of ± 0.2 kcal./mole.

Experimental

Preparation and Purification of Materials.—Baker and Adamson iodine was resublimed three times and stored in a desiccator over phosphorus pentoxide.

Fischer Spectroanalyzed carbon tetrachloride was employed as solvent in all measurements made.

Dimethylbenzamide was prepared by adding benzoyl-chloride dissolved in ether dropwise and with stirring to an ether solution saturated with dimethylamine at 0°. Following the addition of the acid chloride excess dimethyl-

(1) General Electric Foundation Predoctoral Fellow, 1961–1962; abstracted in part from the Ph.D. Thesis of Robert L. Carlson, University of Illinois (1962).
(2) R. S. Drago, R. L. Carlson, N. J. Rose and D. A. Wenz, J. Am. Chem. Soc., 83, 3572 (1961).
(3) N. J. Rose and R. S. Drago, ibid., 81, 6138 (1959).
(4) J. A. A. Ketelaar, et al., Rec. trav. Chim., 71, 1104 (1952).
(5) This research is concerned with an evaluation of K from the overlapping iodine and blue shift complex peaks. The difference in

molar absorptivity of the complex ϵ_C, and iodine ϵ_I is required. See ref. 3.

amine was bubbled through the solution. The ammonium salt was then filtered off, the ether solution extracted with water and dried over anhydrous magnesium sulfate. The ether was distilled off and the amide crystallized from an ether-pet ether mixture. Recrystallization gave a white crystalline solid, m.p. = 45.5–46.0°.

Anal. Calcd. for $C_9H_{11}NO$: C, 72.45; H, 7.43; N, 9.39. Found: C, 72.45; H, 7.36; N, 9.14.

Apparatus.—Spectrophotometric measurements were made with a Beckman DU Spectrophotometer. A forced air heating system employing a thermistor circuit to turn the heater on and off was used to control the temperature. Temperature control of ± 0.1° could be obtained and no detectable temperature gradients were observed in the 1 cm. sample cell.

All measurements of the difference in absorbance between an iodine solution A^0 and an iodine–amide mixture A were obtained directly by placing an iodine solution in the reference cell and the mixture in the sample cell.[6] The concentrations at the various temperatures were corrected for volume changes of the solvent.

Measurement of Spectra.—The spectra shown in Fig. 1 were obtained by measuring the absorbance of the same solution at two different temperatures. The same solution was employed to minimize the effect of errors in concentration due to weighing and pipetting operations.

The data in Table I were obtained at 25.0° and 520 mμ. Calculations were made by using a modified version[4] of the Ketelaar equation

$$\frac{C_I}{A - A^0} = \frac{1}{K(\epsilon_C - \epsilon_I)}\frac{1}{C_A} + \frac{1}{\epsilon_C - \epsilon_I} \quad (1)$$

where C_I is the initial iodine concentration, C_A is the initial amide concentration, $A - A^0$ is the difference in absorbance between the reference iodine solution and the iodine–amide mixture and $(\epsilon_C - \epsilon_I)$ is the difference in the molar absorptivities of the complex and free iodine. K is determined by a least squares calculation of the slope of the line obtained by plotting $C_I/A - A^0$ vs. $1/C_A$. The error is reported at the 90% confidence level.

In Table II the results of a study of the change in the measured value for the enthalpy with change in wave length are reported. Each enthalpy measurement was determined from a single solution of concentration C_I and C_A. The absorbance, $A - A^0$, was measured as a function of temperature over the region 25 to 45° for each solution. K is calculated at different temperatures by assuming that the value of $\epsilon_C - \epsilon_I$ determined at 25° is constant at all temperatures and employing the equation[3]

$$1/K = \frac{C_I C_A}{(A - A^0)}(\epsilon_C - \epsilon_I) - (C_I + C_A) \quad (2)$$

Values of $\epsilon_C - \epsilon_I$ for different wave lengths were calculated by substituting $K = 3.8$ into equation 2 along with the pertinent experimental data obtained at 25°. At 520 mμ the value of -686 (Table I) was employed. Since there is only one correct enthalpy for this system, variation outside experimental error in the calculated enthalpy is indicative of a changing $\epsilon_C - \epsilon_I$.

The data given in Table III was obtained by pipetting 5, 10 and 20 ml. aliquots of an amide solution into separate flasks, adding a given amount of iodine to each and diluting to volume. The absorbance difference, $A - A^0$, was observed at four different temperatures, on each solution in turn. After each solution was studied, the absorbance difference was redetermined at the lowest temperature in order to insure that reaction had not taken place during the course of the experiment. This procedure was employed so that $\epsilon_C - \epsilon_I$ and K could be determined at different temperatures with a minimum number of solutions and weighings thus reducing possible sources of error. By working with the same solution at different temperatures an accurate estimate of relative changes in $\epsilon_C - \epsilon_I$ can be obtained.

Results

The equilibrium constant and molar absorptivity for the adduct of DMB with iodine were determined at 25.0° and 520 mμ. Data are reported in Table I.

(6) Sister M. Brandon, O.P., M. Tamres and S. Searles, *J. Am. Chem. Soc.*, **82**, 2129 (1960).
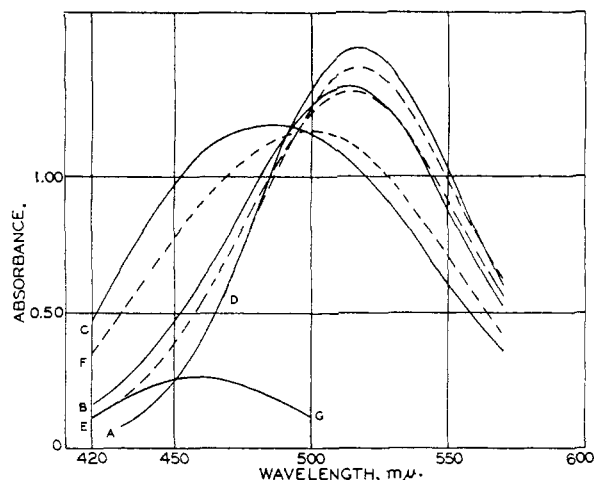

Fig. 1.—Change in the iodine plus complex curves with temperature: A, 0.00157 M I_2; B, 0.00157 M I_2 plus 0.0378 M DMB; C, 0.00157 M I_2 plus 0.1890 M DMB; D, 0.00153 M I_2; E, 0.00153 M I_2 plus 0.0369 M DMB; F, 0.00153 M I_2 plus 0.1843 M DMB; G, resolved complex curve for B.

The results of enthalpy experiments at different wave lengths are reported in Table II. As will be discussed later, it is felt that the best enthalpy value for this system is -4.0 ± 0.2 kcal./mole. Reported enthalpies in Table II differing from this value result at wave lengths where $\epsilon_C - \epsilon_I$ changes with temperature.

TABLE I

DATA AND EQUILIBRIUM CONSTANTS OBTAINED FOR DMB:I_2 AT 25.0° AND 520 mμ

$K = 3.8 \pm 0.1$ $\epsilon_C - \epsilon_I = -686 \pm 16$

C_I	C_A	$-(A - A^0)$
0.001833	0.0393	0.164
.001833	.1967	.538
.001833	.0365	.154
.001833	.1826	.518
.001833	.1657	.491
.001630	.0506	.183
.001630	.2528	.553
.001300	.0587	.163
.001300	.2202	.407
.001300	.2936	.466

TABLE II

DATA OBTAINED AT DIFFERENT WAVE LENGTHS AND ΔH VALUES CALCULATED ASSUMING A TEMPERATURE INDEPENDENT $\epsilon_C - \epsilon_I$

λ	C_I	C_A	$\epsilon_C - \epsilon_I$	$-\Delta H_{calcd.}$
430	0.001741	0.03783	858	4.1
440	.001741	.03783	1018	4.1
450	.001741	.03783	1107	4.0
460	.001741	.03783	1045	4.4
466	.001445	.04808	954	3.8
470	.001741	.03783	849	3.8
472	.001445	.04808	799	3.9
476	.001445	.04808	665	3.5
520	.001714	.07392	−686	4.8 (4.5[a])
550	.001741	.03783	−605	3.9

[a] Correction made for change of ϵ_I with temperature at 520 mμ.

In an attempt to measure directly the change in molar absorptivity $\epsilon_C - \epsilon_I$, with temperature, K and

$\epsilon_C - \epsilon_I$ were determined at 520 mμ at various temperatures. This wave length was selected for the largest deviations would be encountered here (see Table II). A decrease in $\epsilon_C - \epsilon_I$ at 520 mμ is observed as the temperature is increased (Table III). If the molar absorptivities are assumed to be constant as was done for the calculations reported in Table II, the enthalpy calculated will be too large.

TABLE III
EQUILIBRIUM CONSTANTS OBTAINED AT 520 mμ AT DIFFERENT TEMPERATURES USING THREE DIFFERENT AMIDE SOLUTIONS

Temp., °C.	C_I	C_A	K	$-(\epsilon_C - \epsilon_I)$
25.0	0.001225	0.2937	3.91	677
		.1468		
		.0734		
31.4	.001216	.2914	3.45	655
		.1457		
		.0728		
36.9	.001207	.2893	3.06	640
		.1447		
		.0723		
44.6	.001196	.2866	2.54	634
		.1433		
		.0717		

$$\Delta H = -4.1 \pm 0.5$$

(This error is calculated at the 90% confidence level)

In an attempt to ascertain the species which change molar absorptivities with temperature the spectra of iodine were examined. The literature contains conflicting reports concerning the effect of temperature variation of the order of magnitude encountered here on the molar absorptivity of iodine.[7,8] In this study, the spectra of an iodine solution in carbon tetrachloride were obtained at 24.1° and 45.5°. A single solution was employed to eliminate concentration errors. A variation in ϵ_I with temperature is indicated. As would be expected theoretically, the peak decreases in height at the maximum and increases in the wing areas as the temperature is increased. Molar absorptivity values at the two temperatures are summarized in Table IV.

Discussion

Uncertainty exists in the literature concerning the change in molar absorptivity, $\epsilon_C - \epsilon_I$, with temperature differences in the range 20 to 45°. In a recent review on iodine adducts,[9] it was suggested that there is no change in ϵ_C with temperature if a 1:1 adduct forms. In this study definite evidence has been obtained to indicate that the quantities ϵ_C and ϵ_I both change in this temperature range at certain wave lengths. Furthermore, it is demonstrated that the change in molar absorptivity causes appreciable error in the enthalpy determination by our procedure if improperly employed.

The differences in the enthalpy values reported in Table II from the correct value of -4.0 are at-

(7) P. A. D. DeMaine, J. Chem. Phys., 26, 1192 (1957).
(8) H. A. Liebhafsky, J. Am. Chem. Soc., 61, 3513 (1939).
(9) L. J. Andrews and R. M. Keefer, "Advances in Inorganic and Radiochemistry," Vol. III, Academic Press, Inc., New York, N. Y., 1961. p. 123.

TABLE IV
MOLAR ABSORPTIVITY OF IODINE AT 24.1 AND 45.5°

	$T = 24.1°$		$T = 45.5°$
λ	ϵ_I	λ	ϵ_I
420	20	420	22
430	44	430	47
440	81	440	88
450	151	450	156
460	250	460	252
470	380	470	382
480	536	480	531
490	689	490	681
500	824	500	806
510	902	510	881
516	925	516	901
520	921	520	901
530	874	530	859
540	774	540	769
550	642	550	648
560	507	560	520
570	379	570	395
580	269	580	293
590	193	590	207
600	135	600	149
610	97	610	107
620	76	620	83

tributed to changes in $\epsilon_C - \epsilon_I$ with temperature at some wave lengths. Part but not all of this change is due to a decrease in ϵ_I with increasing temperature. When corrections are made on the data at 520 mμ (Table II) for changes in ϵ_I (Table IV), an enthalpy of -4.5 is obtained indicating change in ϵ_C. Further evidence for change in the total quantity $\epsilon_C - \epsilon_I$ with temperature is presented in Fig. 1. The variation in the wave length at which the isosbestic point occurs at the different temperatures is evidence for a changing molar absorptivity. The direction of the change indicates that ϵ_C increases with increasing temperature in the 490 mμ region. Unfortunately, this is the extent of direct information that can be obtained for the complex peak. The change in absorbance of the complex peak cannot be examined in detail as was done for the iodine peak (Table IV). Most of the change in the total absorbance observed (Fig. 1) at the two temperatures for solutions containing complex is due to change in K with temperature. The error existing in K at the two temperatures does not permit accurate enough resolution of the curves of the mixtures to provide information about the change of the entire complex curve with temperature.

Several less direct approaches can be employed to enable accurate calculation of the enthalpy.

(1) The values for K and ΔH can be determined on the free iodine peak at a wave length where changes in the complex absorption are negligible compared to the total absorption. Corrections for changes in ϵ_I with temperature can be employed (Table IV) The wave length best suited for this purpose will vary from one system to another depending upon the magnitude of the blue shift. For the N,N-dimethylbenzamide system, crude resolution of the iodine and complex curve indicates that at 550 mμ, ϵ_C is quite small. The quantity $\epsilon_C - \epsilon_I$ is also large enough that minor changes in ϵ_C will not have an appreciable effect on the

calculated values of ΔH. The ΔH obtained at this wave length is -3.9 ± 0.2 kcal./mole.

(2) The complex maxima occurs around 460 mμ. Since these bands appear to decrease at the maxima and increase in the wing areas with temperature increase, there should be points on either side of the maxima where ϵ does not change with temperature. The constancy of the enthalpy values reported in Table II in the 430 to 450 mμ region and the agreement of these enthalpies with that obtained at 550 mμ indicates that any changes in molar absorptivity with temperature in this region are minor. It is also seen that the percentage change in $\epsilon_C - \epsilon_I$ at 460 mμ is not as great as that at 520 mμ. The enthalpy calculated at 460 mμ assuming no change (Table II) is not as large as that at 520 mμ. This is in part due to the larger value of $\epsilon_C - \epsilon_I$ at 460 mμ.

The changes noted in both ϵ_C and ϵ_I with temperature are in accord with reported behavior and changes expected theoretically. Reportedly the band intensity at the maximum decreases, the absorbance in the wing areas increases and the band area remains constant when the temperature is raised. The arguments presented are in agreement with theoretical prediction and explain both the variation in ΔH with wave length when spectral changes are ignored and the changing wave length for the isosbestic point with temperature increase. The following set of thermodynamic data best describes this system[10]

$$-\Delta F_{298} = 0.79 \pm 0.02 \text{ kcal. mole}^{-1}$$
$$-\Delta H = 4.0 \pm 0.2 \text{ kcal. mole}^{-1}$$
$$-\Delta S = 10.7 \pm 0.7 \text{ e.u.}$$

At 520 mμ and 25° a value of 686 ± 16 is obtained for $\epsilon_C - \epsilon_I$.

The structure of the complex was examined by infrared and ultraviolet spectroscopy. The infrared spectrum indicated a shift of the carbonyl stretching vibration in the adduct to lower wave numbers than that in the free amide. This is evidence for oxygen coördination.[11]

When the heat of association or log K for the DMB adduct is plotted versus σ^* and compared with the plot for a series of aliphatic amides,[12] the DMB value does not fall on the line.

Since the σ^* value employed for these plots is that for a non-conjugated ring, the lack of correlation suggests that the phenyl ring is conjugated with the amide group resulting in a large equilibrium constant and heat of formation for the DMB adduct.

(10) Error limits are imposed at the 90% confidence level.

(11) C. D. Schmulbach and R. S. Drago, J. Am. Chem. Soc., 82, 4484 (1960).

(12) R. S. Drago, R. L. Carlson and D. A. Wenz, ibid., 84, 1106 (1962).

The Kinetics of the Oxidation of Ethanol and of Acetaldehyde by Bromine in Aqueous Solution. Influence of pH

By B. Perlmutter-Hayman and Y. Weissmann

At low and moderate values of pH—at least up to 7.5—the reaction between bromine and acetaldehyde in aqueous solution consists purely in oxidation. The kinetics of the reaction in bromine water show that in the pH range investigated molecular bromine, and not hypobromous acid, is the reactive species in the oxidation of acetaldehyde and of ethanol. The reaction rates increase with increasing pH in a way which agrees quantitatively with the assumption that the anions of alcohol and of acetaldehyde (hydrate) are oxidized much more rapidly than the undissociated molecules—in analogy with the oxidation of formic acid and of d-glucose.

Introduction

The reactions of acetaldehyde[1] and of ethanol[2,3] in bromine water, in the absence of added buffer, consist purely in oxidation. In dilute solution, both reactions are first order with respect to the two reactants.[1,2] In the case of ethanol the situation is somewhat complicated by the presence of two consecutive reactions, the oxidation of ethanol to acetaldehyde, and of acetaldehyde to acetic acid.[2,3] The conditions under which the intermediate, acetaldehyde, reaches a practically constant concentration have been worked out in detail.[3] More recently Kaplan,[4] utilizing the isotope effect, showed that rupture of a C–H linkage is involved in the rate determining step. The suggestion that the hydrogen should be abstracted by the bromine in

the form of a hydride ion[3,4] is supported by a comparison between the kinetic isotope effect in the reaction of bromine water with 2-propan-2-d-ol. and with 1-fluoro-2-propan-2-d-ol.[5]

In buffer solution it was found[3] that at $pH \sim 2.6$ the rate started to increase with increasing pH. The pH effect was not investigated in detail and remained without explanation at the time except that it is not due to the increase in the relative concentration of hypobromous acid.

A similar behavior in the case of formic acid[6,7] and of d-glucose[8] was quantitatively explained on the assumption that the corresponding anions are oxidized at a much higher specific rate than the molecules

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(4) L. Kaplan, ibid., 76, 4645 (1954); 80, 2639 (1958).

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