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Spectroscopic Studies of Keto-Enol Equilibria. VII. Nitrogen-15 Substituted Schiff Bases¹

BY GERALD O. DUDEK AND EMILY PITCHER DUDEK

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A number of Schiff bases were synthesized from methylamine- N^{15} and β -diketones, *o*-hydroxyacetophenones, and *o*-hydroxynaphthaldehydes. The p.m.r. spectra of these adducts confirm previous assignments of structure, and the temperature dependence of the spectra yields information on tautomeric equilibria.

Introduction

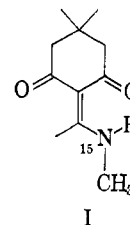
In the preceding papers of this series,¹⁻⁴ p.m.r. studies of the keto-enol equilibria in a variety of Schiff bases derived from β -diketones, *o*-hydroxyacetophenones, and *o*-hydroxyacetophenones have been reported. It appeared that the energy barrier to tautomeric interconversion was large in the aliphatic series, since no proton exchange between sites was apparent. In the 1,2-naphthalene series, the barrier to interconversion was thought to be small with significant exchange of the acidic proton between sites. The N^{14} -quadrupole broadening of the magnetic resonance signals of protons adjacent to the nitrogen, particularly the NH proton, made the interpretation of these spectra difficult.

Proton magnetic resonance studies of amides have shown that N^{15} -substituted compounds can be used to great advantage for studying exchange processes and restricted rotation in nitrogenous systems.⁵ The spin of the N^{15} nucleus is $1/2$, therefore no magnetic quadrupole moment is present.⁵ Furthermore, the N^{15} -H spin coupling constant of 90 c.p.s. permits ready detection of exchange phenomena.

Accordingly, a number of Schiff bases were synthesized using the commercially available methylamine- N^{15} hydrochloride (99% isotopic purity). The compounds were chosen to cover a range of β -diketones and were solids to facilitate handling of small quantities of expensive, isotopic material. To permit readier identification of exchange and tautomeric interconversion,⁷ the spectra were studied not only at the usual spectrometer probe temperature of 31°, but at temperatures to -30° or lower (providing the material would not crystallize out of the solvent). Temperatures above ambient were avoided due to the possibility of reaction between chloroform, the common solvent, and the imine or amine.

Results

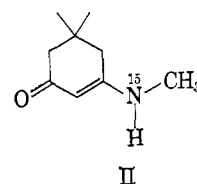
The spectrum of the adduct from methylamine- N^{15} and 2-acetyldimedone (I) is the simplest case to interpret. In contrast to the broad amino hydrogen signal in the spectrum of the N^{14} compound,¹ the amino



resonance of the N^{15} derivative consists of two groups of lines, each group containing a sharp 1:3:3:1 quartet (see Fig. 1 for a similar case). At room temperature ($CDCl_3$ solution), the observed N^{15} -H spin coupling is 88.1 c.p.s., and superimposed on this is a 5.0 c.p.s. coupling from the methyl group. The N^{15} -H coupling is equal to one of the formamide values ($J_{N-H} = 88$ c.p.s.) where exchange is more difficult since it is necessarily intermolecular.⁵ Upon lowering the temperature to -30°, the changes in both the chemical shifts and coupling constants of I are small. Thus exchange processes and intermolecular association effects are of little consequence in this system.

The N^{15} spin coupling to the ethylidene methyl of 2.7 c.p.s. is larger than the coupling to the N-methyl group ($J = 1.6$ c.p.s.). Similarly in tetraethylammonium ions, the N^{14} nucleus is less strongly coupled to the adjacent methylene than to the methyl group.⁸

The N^{15} -substituted 2-(N-methylamino)-5,5-dimethyl-2-cyclohexen-1-one (II) is a slightly more



complex system (Fig. 1). The N^{15} -H spin coupling is 94.3 c.p.s. with a coupling of 4.9 c.p.s. superimposed (from the methyl group). The N^{15} nucleus is spin coupled to the methyl group with $J = 1.2$ c.p.s., this value again being smaller than the longer range coupling to the vinyl group ($J = 1.9$ c.p.s.). As is apparent in Fig. 1, there is a broadening of one of the methylene signals due to an unresolved coupling with the N^{15} nucleus (the two methylene signals are equally sharp in the N^{14} derivative).

As the sample temperature is lowered, the position of the amino hydrogen signal moves markedly downfield (Table I). This is most likely due to intermolecular association of the amino group of one molecule with the carbonyl group of another. Concomitant with this association, the methyl quartet is broadened

(1) Part VI: G. Dudek and G. Volpp, in press.

(2) G. Dudek and R. H. Holm, *J. Am. Chem. Soc.*, **84**, 2691 (1962).

(3) G. Dudek, *ibid.*, **85**, 694 (1963).

(4) G. Dudek and G. Volpp, *ibid.*, **85**, 2697 (1963).

(5) B. Sunners, L. H. Piette, and W. G. Schneider, *Can. J. Chem.*, **38**, 681 (1960).

(6) W. B. Moniz and H. S. Gutowsky, *J. Chem. Phys.*, **38**, 1155 (1963).

(7) In this article, exchange will refer to proton exchange with other molecules either of the same species or chance impurities, while tautomeric interconversion will refer to intramolecular exchange of the proton between sites. Since the spectra of many of these molecules were little altered when reagent pyridine was the solvent³ (one seldom completely water free), it is believed that proton exchange between molecules is negligible.

(8) E. Bullock, D. G. Tuck, and E. J. Woodhouse, *J. Chem. Phys.*, **38**, 2318 (1963).

TABLE I
 PROTON MAGNETIC RESONANCE DATA FOR N¹⁵-SUBSTITUTED SCHIFF BASES^a

Compound	Temp., °C.	NH signal				
		N-Methyl	Other ^g	δ	N ¹⁵	Other couplings
I	31	3.09 (5.1, 1.6) ^b	M 2.57 (2.7) ^b	13.34	88.1 ^b	5.0 ^b
	0	3.10 (5.1, 1.6)	2.57 (2.8)	13.36	88.1	5.1
	-28	3.10 (5.1, 1.6)	2.61 (2.8)	13.36	88.4	5.1
II	31	2.80 (4.9, 1.2)	V 5.05 (1.9)	6.43	94.3	4.9
	0	2.80 (4.7)	5.05 (1.8)	6.94	94.4	5.0
	-30	2.81 (4.0)	5.05 (1.5)	7.37	95.1	4.8
III	31	2.94 (5.3, 1.6)	M 2.00 (2.2)	11.31	91.3	5.3
			V 5.66 (7) ^c			
	0	2.95 (5.4, 1.6)	M 2.00 (2.1)	11.31	91.3	5.2
			V 5.68 (3.6)			
	-30	2.95 (5.4, 1.6)	M 2.01 (2.2)	11.35	91.6	5.3
		V 5.70 (3.6)				
IV	50	3.03 (3.4)	M 2.19 (2.4)	15.92	76.9	4.6
	31	3.01 (4.7, 1.6)	2.17 (2.4)	15.86	79.1	4.7
	15	2.99 (4.6, 1.6)	2.17 (2.4)	15.79	80.3	4.8
	31 ^e	3.05 (4.4, 1.4)	2.22 (2.5)	15.95	77.4	4.6
V	31	3.27 (4) ^f	A 8.57 (6.1)	14.29	64.5	...
	0	3.24 (3.2)	8.50 (9.6)	14.20	72.3	9.8, 4.6
	-30	3.21 (4.7, 1.3)	8.46 (11.0)	14.09	78.4	10.9, 4.7
	-45	3.19 (4.7, 1.4)	8.44 (11.2)	14.02	81.4	11.2, 5.1
	31 ^e	3.10 (4) ^c	...	14.78	58.2	...
	31 ^f	3.27 (4.4) ^c	8.62 (5.8)	14.35	61.5	...
VI	31	3.24 (2.5) ^e	M 2.23 (1.8, 0.8)	15.41 ^d	(6) ^c	...
	0	3.21 (2.4) ^c	2.21 (1.9, 0.8)	15.77 ^d	(4) ^c	...

^a CDCl₃ solvent (exception noted) in p.p.m. downfield from tetramethylsilane at 60.00 Mc. ^b In c.p.s. ^c Peak width at half-peak height. ^d Hydroxyl signal. ^e Pyridine solvent. ^f Methylene chloride solvent. ^g M = methyl signal, V = vinyl signal, A = aldehyde signal.

such that the N¹⁵-CH₃ spin coupling ($J = 1.2$ c.p.s.) is no longer observable. The change in the observed spin coupling of the methyl group is in part due to the averaging of the two couplings produced by the broadening (Table I). The N¹⁵-H coupling and the NH-CH₃ coupling (measured in the NH signal) are little affected by the association. In this case, the amino hydrogen signal is a better measure of the methyl coupling.

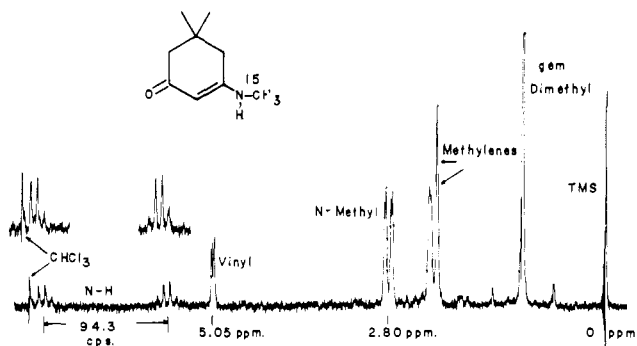
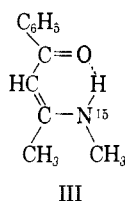


Fig. 1.—The p.m.r. spectrum (in CDCl₃ at 60.00 Mc.) of 3-(N-methylamino)-5,5-dimethyl-2-cyclohexen-1-one-N¹⁵. The NH signals are repeated at a higher spectrum amplitude.

The spectrum of N¹⁵-substituted 3-(N-methylimino)-crotonophenone (III) is similar to I and II. The

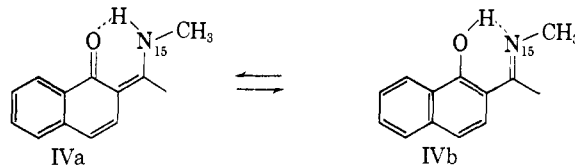


trans N¹⁵-vinyl coupling of 3.6 c.p.s. is much larger than the *cis* value of 1.9 c.p.s. in II, while the $J_{N^{15}-H}$

coupling of 91.3 c.p.s. is larger than the 88 c.p.s. value in compound I.

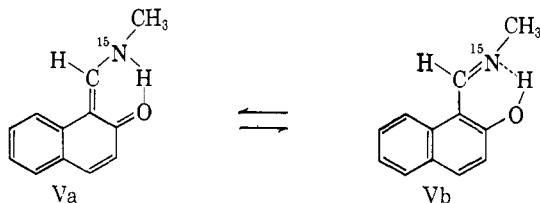
The difference in $J_{N^{15}-H}$ between I, II, and III need not reflect a variation in tautomeric interchange. According to Sunners, *et al.*,⁵ the spin coupling constant may vary somewhat with NH bond length and hybridization of the nitrogen.

The p.m.r. spectrum in deuteriochloroform of N-methyl-1-hydroxy-2-acetonaphthone imine-N¹⁵ indicates that, in agreement with earlier assignments,³ the compound is mainly in the keto-amine form IVa. The NH coupling is smaller than the one observed in the aliphatic compounds and increases slightly upon



lowering the temperature to 15° (from $J = 79.1$ to 80.3 c.p.s.). Unfortunately, the solubility limit of the compound in deuteriochloroform is approximately 10° for the concentrations needed for this study. From the experimentally observed temperature range, tautomeric interchange is present at 31°, but the amount of IVb is not large. If $J \approx 88$ c.p.s. is assumed as the hydrogen-bonded NH-coupling value, then about 10% IVb is present at 31°. At 50°, exchange or tautomeric interconversion is more significant.

The spectra of N-methyl-2-hydroxy-1-naphthaldehyde imine-N¹⁵ (V) are a good illustration of the effect of tautomeric interconversion. At 31°, the NH signal consists of two broad peaks with a spacing of 64.5 c.p.s. (from the N¹⁵-H coupling). The aldehyde signal is a broad 6.1 c.p.s. doublet and the methyl signal is a



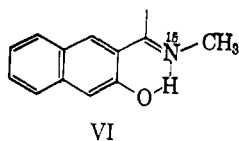
singlet with a width at half-peak height of 4 c.p.s. (see Fig. 2). When the sample temperature is lowered to 0°, the spectrum alters markedly. The observed N¹⁵-H coupling increases to 72.3 c.p.s., and the longer range couplings from the aldehyde and methyl protons are observable as two overlapping 1:3:3:1 quartets. The aldehyde resonance is a 9.6 c.p.s. doublet, while the methyl is a 3.2 c.p.s. doublet (Fig. 2). At -30°, the second coupling of 1.3 c.p.s. is now apparent in the methyl group resonance; this coupling is due to the N¹⁵ nucleus. The material is still in solution at -45°, but viscosity broadening is noticeable as indicated by the TMS line width.

In addition to the major alterations in the spectrum as the sample temperature is lowered, there are several smaller changes worthy of note. The spectrum of 2-acetyldimedone imine (I) suggests that dependence of the various chemical shifts upon temperature is small. In the aldehyde system (V), the acidic hydrogen is shifted 0.27 p.p.m. upfield upon lowering the temperature to -45°. This shift is opposite to the one expected from either association or a stronger hydrogen bond. The same shift is seen in the acidic proton of the hydroxyacetonephthalone imine (IV). These shifts could reflect the condition that the more nearly the equilibrium between tautomers approaches unity, the more paramagnetic the resonance of the enolic proton.

It is interesting that even at the two lowest temperatures, the aldehyde signal indicates the presence of only a small N¹⁵ coupling, it being less than 1 c.p.s. (from an estimate of the line broadening). In formamide, the N¹⁵-aldehyde coupling ranges from $J = 2.1$ (*cis*) to 12.9 c.p.s. (*trans*).⁵

The utility of the N¹⁵-H couplings for the determination of tautomeric equilibria is apparent when pyridine was used as the solvent for compound V. The methyl signal of V (at 31°) is unaffected by any differences between chloroform and pyridine (a 4 c.p.s. wide singlet in both solvents). The aldehyde proton is obscured by the residual protium signal from the deuteriopyridine. The N¹⁵-H coupling, however, readily indicates that the tautomeric equilibrium is similar in both solvents (the equilibrium favoring Va).

The aromatic compound, N-methyl-2-hydroxy-3-acetonaphthalone imine-N¹⁵ (VI) possesses a simple p.m.r. spectrum. The hydroxyl resonance is ~6



c.p.s. wide at 31°, but sharpens slightly at 0° (~4 c.p.s. wide). Unfortunately, the solubility of the compound in chloroform precludes lowering the temperature below 0°. The temperature dependence of

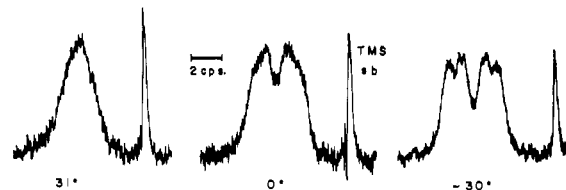


Fig. 2.—The methyl resonance signal (at 60.00 Mc. in CDCl₃) of N-methyl 2-hydroxy-1-naphthaldehyde imine-N¹⁵ as a function of sample temperature. A side band of tetramethylsilane (generated by an audio oscillator) is included for purposes of comparison.

the chemical shift of the acidic proton is opposite to that shown by this proton in compounds IV or V.

The ethylidene methyl-N¹⁵ coupling is 1.9 c.p.s. and a methyl-methyl interaction is present with $J = 0.8$ c.p.s. (also observed in the N¹⁴ compound). Since the N-methyl signal is 2.5 c.p.s. wide at half-peak height, when the 0.8 c.p.s. methyl-methyl coupling is subtracted, the maximum possible value of the N¹⁵-methyl coupling is less than 1 c.p.s.

Experimental

P.m.r. Spectra.—The spectra were taken on a Varian A-60 spectrometer operating at 60.00 Mc. Tetramethylsilane was used as the internal standard, and all chemical shifts were given in p.p.m. downfield from this origin. The spectra were calibrated by interpolation from side bands generated by an audio oscillator. The audio oscillator was continuously monitored by a frequency counter. The chemical shifts are accurate to better than 0.01 p.p.m. (0.6 c.p.s.); spin coupling constants are accurate to 0.2 c.p.s. unless otherwise specified. The variable temperature probe was calibrated by measuring the separation between the hydroxyl and methyl signals of methanol. The separation was converted to temperature with the conversion chart supplied by Varian Associates. The temperature is good to $\pm 2^\circ$.

The deuteriochloroform and deuteriopyridine were supplied by Merck Sharp and Dohme of Canada. All samples were about 1 M and were vacuum degassed. As a precaution, the samples were stored in liquid nitrogen until measured.

Compounds.—The compounds were prepared as previously described¹⁻⁴ except on a 1-mmole scale. The physical properties agreed with those previously given. The methylamine-N¹⁵ hydrochloride (99% isotopic purity) was supplied by Merck Sharp and Dohme of Canada.

Discussion

Several advantages accrue in using N¹⁵ compounds for p.m.r. studies of tautomeric systems. The broadening effect of the N¹⁴ quadrupole moment is eliminated, and the large N¹⁵-H spin coupling permits ready detection of tautomeric interconversion and exchange processes as illustrated by several examples described herein. In addition to the information on tautomeric equilibria, the N¹⁵ derivatives provide verification of the correctness of the structure proposed. For example, in an earlier paper of this series,² it was claimed that addition of an amine to 2-acetyldimedone resulted in the symmetrical structure I rather than the compound which results from nitrogen attack on a ring carbonyl. The presence of the ethylidene methyl coupling to the N¹⁵ nucleus and the absence of the N¹⁵-methylene interaction (seen in II) is further confirmation of the symmetrical structure.

In the case of compounds similar to III, the structure of the adduct has been disputed. The attack by an amine on the parent β -diketone could be either at the carbonyl adjacent to the phenyl or at the one adjacent to the methyl group. On the basis of dipole

moment studies, McCarthy and Martell⁹ concluded the attack by an amine was at the phenyl carbonyl, resulting in a Schiff base with an aceto function still present. On the other hand, the differential solvent shift of the methyl resonance, using benzene as the second solvent, suggested that a benzoyl grouping was present, similar to compound III.¹⁰ The presence of the N¹⁵ coupling to the methyl group confirms the previous proton resonance studies, and the structure of the molecule is correctly given as III.¹¹

An alternative structure can be proposed for the adduct between an amine and 1-hydroxy-2-acetonaphthone in lieu of IVa or IVb. An amine may attack the hydroxyl group of the naphthalene rather than the carbonyl of the side chain. The product would then be a 1-amino-2-acetonaphthone instead of the expected 1-hydroxy-2-acetonaphthone imine. Again the presence of the N¹⁵ coupling to the ethylidene methyl favors the product from the carbonyl attack (V).

It may be argued that the observed N¹⁵-H couplings in some of the Schiff bases are the result of "through space" couplings¹²; that is, the hydrogen bond which holds the N¹⁵ nucleus and the hydroxyl proton in close proximity permits spin-spin interactions without any formal bond and without the electron redistributions in the aromatic rings required by IVa or Va. Although "through space" coupling is seldom considered in describing proton-proton spin coupling, it has been invoked in fluorine-fluorine spin couplings.¹²

Two arguments are advanced here against this view. In the 2,3-naphthalene derivative (VI), the barrier to tautomeric interconversion is large since quinoid resonance structures are required for the existence of the keto-amine form.³ The N¹⁵-H spin coupling is not observed in this compound. The 1,2-aldehyde (V) and the 1,2-acetonaphthone (IV) are both claimed to exist in the keto-amine tautomer since large N¹⁵-H couplings occur in both compounds. If the presence of "through space" coupling requires the hydrogen bond to hold the system oriented so that nitrogen-hydrogen dipole-dipole averaging cannot occur, then the 2,3-acetonaphthone derivative (VI) is anomalous. Its hydrogen bond strength as determined by the p.m.r. chemical shift is intermediate between that of the 1,2-aldehyde (V) and the 1,2-ketone (IV), even allowing for some variation in ring-current effect on the proton resonance position.

The second argument concerns the magnitude of the N¹⁵-methyl spin coupling. In compounds III, IV, and V, the N¹⁵-methyl coupling is resolved with $J = 1.2$ c.p.s. or larger, whereas in VI, it is less than 0.9 c.p.s. The N¹⁵-ethylidene methyl coupling is usually 2.2-2.7 c.p.s., but in VI it is 1.8 c.p.s. Thus there are distinct differences between these two groups of compounds.¹³

The variation in the coupling constants of the aromatic Schiff bases with both temperature and solvent indicate that tautomeric interconversion is occurring. Consequently, the rate and thermodynamic properties

of the process are of interest. In contrast to earlier views,³ it is believed that the exchange process is *rapid* with a very low activation energy.

If the exchange rate of the proton in the aromatic Schiff base is slow, it should be possible to detect both tautomers in the p.m.r. spectrum. In particular, the large N¹⁵-H coupling should allow the detection of the imine tautomer since compound IV, for example, should contain about 10% of the imine form at room temperature.¹⁵ The hydroxyl proton signal would be a singlet with a large apparent amplitude as compared to the complex NH signal. Since no trace of the imine form appeared in the p.m.r. spectrum, we consider this support for rapid interconversion.

The situation with the aromatic Schiff bases is entirely analogous to that of the hydroxymethylene ketones reported by Garbisch.¹⁶ With the ketones, the small change in the equilibrium position of the enol proton was likewise considered a low-activation-energy process. Garbisch further pointed out that as long as proton transfer between sites is *intramolecular*, rapid proton exchange need not necessarily cause spin averaging.

In fast exchange, the observed spin coupling constant (J_{obsd}) is given by a weighted average of the various coupling constants involved,¹⁷ in this particular case, J_O (the coupling constant for the proton attached to oxygen) and J_N (the coupling constant for the proton attached to nitrogen-15).

$$J_{\text{obsd}} = J_O p_O + J_N p_N$$

Since $J_O = 0$ and only two sites for the proton are involved ($p_O + p_N = 1$), the observed coupling of the acidic proton is a measure of the oxygen-nitrogen equilibrium (K).

If J_N is set equal to 88 c.p.s., plots of $\ln K$ vs. $1/T$ ($^{\circ}\text{K.}$) for compounds IV and V are linear over the experimentally available temperature range (in one case 75°). With V, several values of J_N were tried, but 88 c.p.s. yielded the most linear plot. This value of the coupling constant is the observed value for compound I and is also that for several of the formamide couplings.⁵ An argument could be made for using a larger value of J_N , so the values given in Table II are subject to some uncertainty.

TABLE II
- ΔH FOR THE AMINE-IMINE EQUILIBRIUM

Solvent	$-\Delta H, \text{kcal.}$		
	IV ^a	V ^a	V ^b
CDCl ₃	2.3	2.7	2.4
CH ₂ Cl ₂	2.0	1.9	1.9
Pyridine- <i>d</i> ₅	...	1.8	1.8

^a $J_N = 88$ c.p.s. ^b $J_N = 90$ c.p.s.

The data in Tables I and II suggest that keto-amine forms of the aromatic Schiff bases are strongly stabilized by association with the solvent. The magnitude of ΔH is reasonable for such a solvent effect, especially the higher values for chloroform. Unfortunately, the low solubility of these compounds in inert solvents limits the extent of this study.

(15) The ultraviolet spectrum of IV (in chloroform) indicates the presence of a small amount of the imine tautomer.¹⁴

(16) E. Garbisch, *J. Am. Chem. Soc.*, **85**, 1696 (1963).

(17) D. Graham and J. S. Waugh, *J. Chem. Phys.*, **27**, 968 (1957);

(9) P. J. McCarthy and A. E. Martell, *J. Am. Chem. Soc.*, **78**, 264 (1956).

(10) G. Dudek and R. H. Holm, *ibid.*, **83**, 2099 (1961).

(11) We wish to thank Mr. Grover Everett for requesting confirmation of the structure of this molecule.

(12) S. Ng and C. H. Sederholm, *J. Chem. Phys.*, **40**, 2090 (1964).

(13) The ultraviolet spectra of these molecules are in agreement with this view that VI is electronically different from IV or V.¹⁴

(14) G. Dudek and E. P. Dudek, unpublished work.

The simple Hückel molecular orbital calculations obtained for the aliphatic Schiff bases indicate that the system is polar with an appreciable negative charge on oxygen and with a partially delocalized positive charge.⁴ The same situation probably occurs in the aromatic Schiff bases IV and V with the possibility of delocalizing the charge into the aromatic system. In the enol-imine form, the charge distri-

bution calculated for the aliphatic system suggests the system is less polar than the keto-amine form, primarily owing to the removal of the highly dipolar carbonyl group. The carbonyl oxygen would be a logical site for association with a hydrogen bonding solvent such as chloroform.

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[CONTRIBUTION FROM THE DEPARTMENT OF PHYSICAL CHEMISTRY, HEBREW UNIVERSITY, JERUSALEM, ISRAEL]

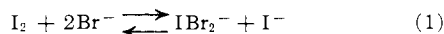
A Spectrophotometric Study of the System $I_2 + Br^-$

BY EHUD EYAL AND AVNER TREININ

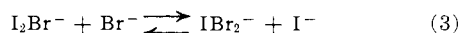
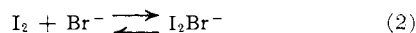
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The ultraviolet spectrum of the system $I_2 + Br^-$ was thoroughly investigated. The shift of the main absorption band to shorter wave lengths on raising the concentration of Br^- is ascribed to the equilibrium: $I_2Br^- + Br^- \rightleftharpoons IBr_2^- + I^-$. The spectroscopic and thermodynamic properties of the two complexes involved were determined. The origin of the electronic transitions is discussed.

Solutions containing I_2 and Br^- exhibit an intense absorption band, the location of which depends markedly on the concentration of Br^- .^{1,2} Thus on raising the concentration of Br^- from 2×10^{-3} to 3 M, the peak of the band is shifted from 270 to 256 m μ .¹ The spectrum at low Br^- concentration was assigned to I_2Br^- , this assignment being in agreement with the proposed origin of the band,¹ but the nature of the spectral shift on raising the bromide concentration remained unclear. The spectrum of IBr_2^- in aqueous solution displays an intense band at about 254 m μ .³ Therefore, Daniele² proposed that the spectral shift is due to IBr_2^- , which he considered to be photochemically produced in concentrated bromide solutions. However, we found the same spectral shifts irrespective of room and spectrophotometric illumination, so this cannot be the correct answer. But IBr_2^- is normally produced in $I_2 + Br^-$ solutions as expressed by the equilibrium



or



From the available thermodynamic data,⁴ we obtain at 25°

$$K_3 = \frac{(IBr_2^-)(I^-)}{(I_2Br^-)(Br^-)} = 1.4 \times 10^{-4} \quad (4)$$

which shows that when $(Br^-)/(I^-)$ is $\sim 10^6$, practically no complex but IBr_2^- is present in solution.

In this work we present the results of a detailed spectrophotometric study of the system $I_2 + Br^-$, from which we derive the spectra and some thermodynamic properties of I_2Br^- and IBr_2^- .

Experimental

The absorption spectra were measured for (a) iodine in solutions of NaBr at various concentrations; (b) the same, but

(1) D. Meyerstein and A. Treinin, *Trans. Faraday Soc.*, **59**, 1114 (1963).

(2) G. Daniele, *Gazz. chim. ital.*, **90**, 1082 (1960).

(3) A. E. Gillam, *Trans. Faraday Soc.*, **29**, 1132 (1933).

(4) W. M. Latimer, "Oxidation Potentials," Prentice-Hall, Inc., Englewood Cliffs, N. J., 1952.

with addition of a relatively small concentration of NaI; (c) IBr in solutions of 0.02 M HClO₄ and various concentrations of NaBr; (d) IBr in 10 M HClO₄ and a small concentration of NaCl. The spectrophotometric measurements were carried out with a Hilger Uvispek spectrophotometer in a thermostated cell compartment ($\pm 0.5^\circ$); 1-cm. silica cells were used.

Materials.—NaBr, NaI, and HClO₄ of A.R. grade were used without further purification. Resublimed I₂ was further sublimed. To prepare IBr we added excess of Br₂ (A.R.) to I₂ and kept the mixture at 50° for several hours. The IBr was sublimed from this mixture and its purity checked by determining its melting point (41°). Solutions of freshly sublimed IBr were used, but nevertheless they always appeared to contain excess I₂ (see Results). Water was redistilled from alkaline permanganate and from dilute phosphoric acid in an all-glass still.

Solutions.—The solutions of sets a and b were prepared from a saturated stock solution of I₂ and solutions of NaBr and NaI. At the end of each measurement, the total concentration of the iodine was determined by adding few crystals of KI to the solution and measuring the absorbance of I₃⁻ at 352 m μ .¹ We confirmed that this absorbance was independent of further addition of KI. The solutions of set c were prepared by dissolving about 50 mg. of IBr in 1 M NaBr solutions and then diluting by a factor of 1/500. This procedure was used in order to rapidly dissolve the IBr. The dilute solution of IBr was used as a stock solution for preparing the mixtures, which contained HClO₄ to prevent hydrolysis. The exact concentration of IBr was determined in the same way as done for I₂, but now the excess of KI was added to a blank solution containing the same concentrations of IBr and NaBr but with no HClO₄ present. This was done to prevent autoxidation of I⁻. The solutions of set d were prepared by adding few crystals of NaCl to solutions of IBr in 10 M HClO₄.

Results

On raising the Br^- concentration at constant I₂ concentration ($\sim 10^{-5}$ M), the peak of the absorption band is gradually shifted from 270 to 254 m μ . The apparent extinction coefficient, $\bar{\epsilon}_{\max} = D_{\max}/(I_2)_0$ [(I₂)₀ is the total concentration of iodine] increases thereby till it reaches a constant value of 5.4×10^4 (Fig. 1). The following preliminary experiments seem to prove that the 270-m μ band is due to I_2Br^- , which is converted to IBr_2^- on raising the Br^- concentration.

a. Job's method of continuous variations⁵ tested on 10^{-3} M solutions of I₂ and NaBr indicate the formation of a 1:1 complex (Fig. 2).

(5) P. Job, *Ann. chim.* (Paris), **9**, 113, 135 (1928). It should be realized that the use of equal concentrations of reactants is not essential provided only a little of both reactants enters into the complex.