

arranged in a series according to their ability to cause d-orbital splitting. This is the so-called spectrochemical series and is the sequence that should be obeyed when metal-ligand interaction is largely electrostatic in origin (crystal field theory). In part, this series is $I^- < Br^- < Cl^- < (C_6H_5)_3PO$. Where the mixing of metal atom orbitals with ligand atom orbitals becomes important, d-electron cloud expansion also must be considered. The relative effect of ligands in expanding the d-electron cloud has been named the nephelauxetic (cloud expanding) series which is, in part, $(C_6H_5)_3PO < Cl^- < Br^- < I^-$.^{22,23} The relationship between this series and assistor activity is apparent. The nephelauxetic effect has also been correlated with the polarizability or covalency of the ligands.²⁴ One could visualize such d-orbital expansion in the present case as resulting from π -antibonding which will increase the charge on the metal atom. Such an effect could also result from the donation of charge to the metal atom by the polarization of the assistor since the observed series of increasing assistor activity does parallel the increasing polarizability and decreasing ionization potential of the series of ligands considered. The result of increased charge on the metal atom is to weaken the M-C bond; the basic arguments involved are to be found in discussions of polarization theory and the so-called *trans* effect. In summary, whatever the source, the effect of covalency is to delocalize (render more diffuse) the electronic distribution around the metal atom and to weaken the carbon-metal bond.

Evidence for this weakening of M-C bonds by coordination has been cited by Brownstein, *et al.*,²⁵ who were able to correlate the nuclear magnetic resonance frequencies of the methyl and methylene hydrogens in triethylaluminum and triethylgallium with the ability of solvent to coordinate with the electron-deficient metal. Increased electron density about the metal atom resulted in a decreased tendency to share electrons in an M-C bond.

The concept of assistance may be a fairly general

(22) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," Interscience Publishers, Inc., New York, N. Y., 1962, p. 593.

(23) D. M. L. Goodgame, M. Goodgame and F. A. Cotton, *J. Am. Chem. Soc.*, **83**, 4161 (1961).

(24) D. W. Meek, R. S. Drago and T. S. Piper, *Inorg. Chem.*, **1**, 285 (1962).

(25) S. Brownstein, B. C. Smith, G. Ehrlich and A. W. Laubengayer, *J. Am. Chem. Soc.*, **81**, 3826 (1959).

phenomenon, since work in these laboratories indicates that the reaction of tributyltin hydride with acetic acid is assisted by halide ion.

The concept also explains a number of facts concerning organometal reactions. For example, it appears that in many organometallic compounds the rate of cleavage of the metal-carbon or metal-hydrogen linkages is not a function of the acidity of the acid used alone but is also related to the ability of the atom to which the hydrogen is attached to coordinate with a metal atom. Coates and Huck²⁶ have reported that the rates of cleavage of dimethylberyllium by active hydrogen compounds is in the order $ROH > R_2NH > RSH$. Organoboron compounds react more rapidly with carboxylic acids than the halogen acids.²⁷

The rate of reaction of $LiBH_4$ with HA increases along the series $C_6H_6, C_4H_5N, t-BuOH, CH_3OH$, as HA is varied, while the K_a 's of the acids increase along the series $C_4H_5N, t-BuOH, CH_3OH, C_6H_6$.²⁸

Finally, Coates has introduced a nearly identical concept to explain the different orientations of cleavage in the reactions $C_6F_5HgR + HCl \rightarrow$, and $C_6F_5HgR + Br_2 \rightarrow$.²⁹

The practical applications of this concept of assistance seem very evident. It should be possible to increase the ability of an organometal to donate a carbanion to a substrate or increase the ability of a metal hydride to donate a hydride ion to a substrate. Finally it is felt that this investigation points out the advantages to be gained by the application of the basic philosophies and nomenclature of the inorganic chemist to the field of reaction mechanisms involving organometallic compounds. A review of the area has been presented by Dessy and Paulik.³⁰

Acknowledgment.—The work reported in this paper was supported by the Army Research Office (USA-DA-ARO-31-412), the Petroleum Research Fund of the American Chemical Society (PRF 417-A), and the National Science Foundation (NSF G-14182).

(26) G. E. Coates and N. D. Huck, *J. Chem. Soc.*, 4512 (1952).

(27) H. C. Brown in "Organometallic Chemistry," Edited by H. Zeiss, ACS Monograph No. 147, Reinhold Publishing Corp., New York, N. Y., 1960, p. 111.

(28) R. E. Dessy and E. Grannen, Jr., *J. Am. Chem. Soc.*, **83**, 3953 (1961).

(29) R. D. Chambers, G. E. Coates, J. G. Livingstone and W. K. R. Musgrave, *J. Chem. Soc.*, 4367 (1962).

(30) R. E. Dessy and F. E. Paulik, *J. Chem. Educ.*, **40**, 185 (1963).

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Basicity of N-Nitrosamines. II.¹ Aqueous Sulfuric Acid Solutions^{2,3}

BY WILLIAM S. LAYNE, HANS H. JAFFÉ AND HANS ZIMMER

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The ultraviolet spectra of dimethyl-N-nitrosamine and diisopropyl-N-nitrosamine were examined in aqueous sulfuric acid solutions and the changes of spectra were observed at a number of acid concentrations. The changes of spectra indicate the N-nitrosamine molecule exists in four spectroscopically distinguishable forms in aqueous acidic solution, with the proportion of each determined by the acid concentration. The first and second equilibrium constants were calculated, and their dependence on acid concentration indicates the reactions producing spectral change are the formation of hydrogen bonds between the N-nitrosamine molecule and sulfuric acid. White, crystalline 1:1 addition compounds of di-n-heptyl-N-nitrosamine, di-n-octyl-N-nitrosamine and bis-(2-ethylhexyl)-N-nitrosamine with perchloric acid were prepared.

In an attempt to measure the base strengths of a series of N-nitrosamines, we have measured the spectra

(1) Part I: *J. Am. Chem. Soc.*, **85**, 435 (1963).

(2) This work was supported by the Office of Ordnance Research, U. S. Army.

(3) Taken in part from the Ph.D. Thesis of W. S. L., University of Cincinnati, 1961.

of such compounds in a series of solutions in aqueous sulfuric acid. Rather than finding the expected simple change due to an acid-base reaction, we observed a complicated series of changes. These complications are reminiscent of the sensitivity of the spectra of N-nitroso compounds to solvents, previously observed by Haszel-

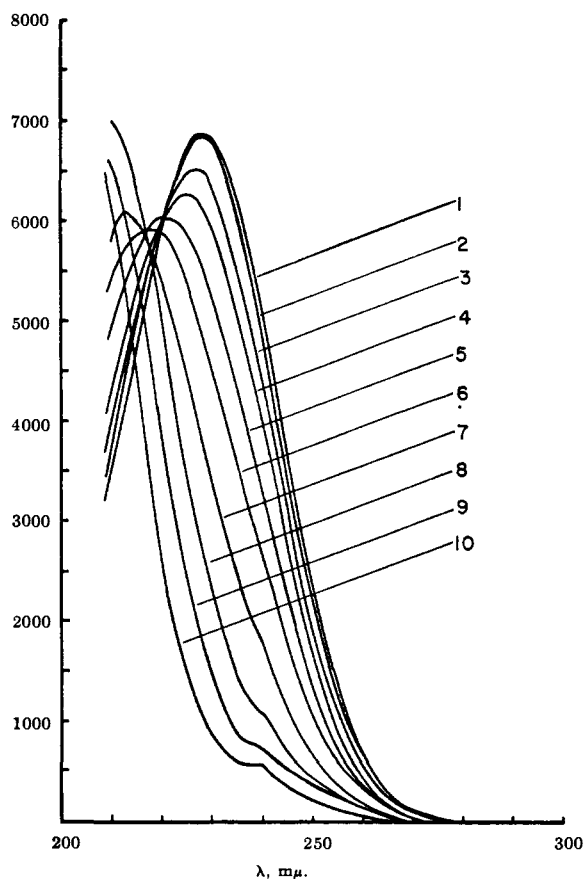


Fig. 1.—Spectra of dimethyl-N-nitrosamine in aqueous sulfuric acid solutions; the acidity increases from solution 1 to solution 10.

dine and Mattinson.⁴ Although a number of mechanisms have been proposed to explain the solvent sensitivity of these spectra, as discussed in part I,¹ little definitive evidence is available concerning their nature with the exception of the evidence for hydrogen bonding in Part I and in the work of Chandra and Basu.⁵ Given the complicated behavior of the spectra of the N-nitrosamines in aqueous sulfuric acid, we have attempted to isolate the various partial processes involved and to elucidate their nature.

In the process of this work, attempts were also made to prepare and characterize N-nitrosamine salts.

Experimental

The N-nitrosamines were available from previous work by the authors⁶; they were purified by distillation under reduced pressure prior to use. Dimethyl-N-nitrosamine was prepared by the method of Renouf.⁷

Solutions were prepared in volumetric flasks by diluting a pipetted or weighed portion of the N-nitrosamine, diluted with solvent as necessary, with a solution of sulfuric acid until approximately the desired amount of acid had been added. The dilution was completed by adding water until the desired total volume was reached. The concentration of acid in each final solution was determined by titrating aliquots with a standard aqueous base solution to the phenolphthalein end-point. All spectra were recorded on a Cary model 11 recording spectrophotometer, using 1-cm. quartz cells.

Discussion

Examination of the spectra of dimethyl-N-nitrosamine solutions disclosed the following facts. The spectrum in aqueous solution has a strong absorption at 228 $m\mu$, assigned to a $\pi \rightarrow \pi^*$ transition (cf. Fig. 1). Also present is a weaker band at 332 $m\mu$ which can be attributed to an $n \rightarrow \pi^*$ transition. The spectrum is the

(4) R. N. Haszeldine and B. J. H. Mattinson, *J. Chem. Soc.*, 4172 (1955).

(5) A. K. Chandra and S. Basu, *Trans. Faraday Soc.*, **56**, 632 (1960).

(6) W. S. Layne and H. Zimmer, to be published.

(7) E. Renouf, *Chem. Ber.*, **13**, 2170 (1880).

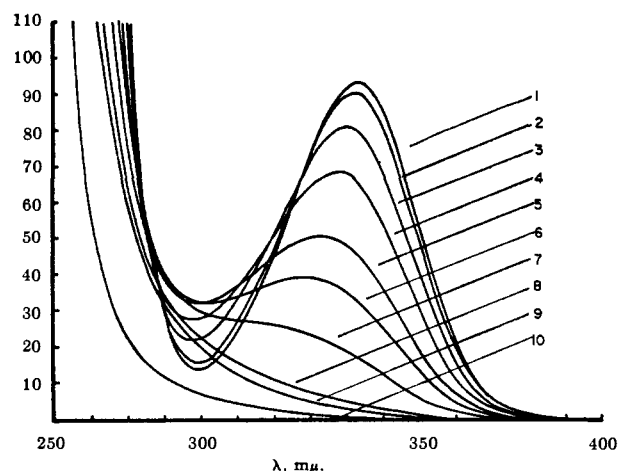


Fig. 2.—Spectra of dimethyl-N-nitrosamine in aqueous sulfuric acid solutions; the acidity increases from solution 1 to solution 10.

same in basic or neutral solutions and in acidic solutions of $pH > 1$, but the intensity of the $n \rightarrow \pi^*$ band decreased rapidly in more acidic solutions and is absent for solutions in concentrated sulfuric acid. Moreover, the reaction with sulfuric acid is reversible, as was shown by diluting with water a solution of dimethyl-N-nitrosamine in concentrated sulfuric acid and comparing its spectrum with that of a solution of the same concentration prepared by adding the N-nitrosamine to a dilute sulfuric acid solution.

The spectrum of dimethyl-N-nitrosamine in water is almost identical with the spectrum graphically reconstructed in part I for the first complex formed of dimethyl-N-nitrosamine in cyclohexane solution with trichloroacetic acid (HTCA). The absorption maximum in aqueous solution is at 332 $m\mu$, compared to about 333 $m\mu$ in the reconstructed curve. While the complex with HTCA in the non-aqueous solution, formulated as $R_2NNO \cdot HTCA$, involves only one hydrogen bond, the molecule in water is undoubtedly extensively solvated by hydrogen bonding, $R_2NNO \cdot (H_2O)_x$. The spectral similarity of these two species is reasonable since additional hydrogen bonds, after the first one, appear to produce successively smaller effects on the spectra, and since the H-bond with HTCA is probably stronger than that with any one H_2O molecule. A single molecule of HTCA is considered to induce an effect on the N-nitrosamine molecule comparable to that produced by the entire aqueous cage surrounding such a molecule.

Spectra were recorded of the N-nitrosamine absorption at a range of wave lengths from 252 to 400 $m\mu$, and at a variety of acid concentrations, and such spectra are shown in Fig. 2 and 3. For dimethyl-N-nitrosamine, examination of these spectra revealed the following important features: (1) an absorption maximum at 332 $m\mu$ for the base in aqueous solution; (2) an absorption minimum at 288 $m\mu$ for the base in aqueous solution; (3) a decrease of intensity of the absorption maximum as acid is added, with complete disappearance of the maximum in concentrated sulfuric acid; (4) an isoabsorptive point at about 275 $m\mu$ for solutions of a molar acid concentration $\leq 5 M$; (5) an increase in the absorption at 288 $m\mu$ as the acid concentration is increased to 5 M ; (6) a decrease of absorption with increasing acid concentration at 288 $m\mu$ over the range 5 to 18 M (concentrated sulfuric acid); and (7) a hypsochromic shift in the long wave length absorption maximum as the acid concentration is increased.

Examination of the spectra in the range of 200 to 280 $m\mu$ shows that the absorption maximum due to the

TABLE I
CALCULATED CONCENTRATION AND EQUILIBRIUM CONSTANTS OF DIMETHYL-N-NITROSAMINE SPECIES IN AQUEOUS SULFURIC ACID SOLUTIONS

Soln.	C_I	C_{II}	C_{III}	C_{IV}	$[H_2SO_4], M$	$\alpha_{H^+}^a$	$K_1 =$	$K_1 =$	$K_2 =$	$K_2 =$
							$\frac{C_I}{C_I \alpha_{H^+}}$	$\frac{C_{II}}{C_I [H_2SO_4]}$	$\frac{C_{III}}{C_{III} \alpha_{H^+}}$	$\frac{C_{IV}}{C_{II} [H_2SO_4]}$
1	0.02024	0	0	0	0	10^{-7}
2	.0184	.00184	0	0	0.70	1.07	0.0935	0.1445
3	.01483	.0045	0.00091	0	2.255	9.55	.0318	.1357	0.0212	0.0897
4	.01104	.00596	.00324	0	3.38	36.3	.0149	.1598	.0150	.1607
5	.00662	.00598	.00764	0	4.51	120.0	.00752	.2002	.01064	.283
6	.00441	.00479	.01104	0	5.26	251.0	.00432	.206	.0092	.439
7	.00190	.00267	.0141	0.00154	6.39	933	.00151	.235	.00566	.826
8	.00018	.000066	.01511	.00487	8.65	16600	.000002	.039	.0138	16.5
9	0	0	.01306	.00718	11.28	1.32×10^6
10	0	0	0	.02024	18.78	10^{10}

^a Computed from tables in M. A. Paul and F. A. Long, *Chem. Rev.*, **57**, 1 (1957), and L. P. Hammett and A. J. Deydrup, *J. Am. Chem. Soc.*, **54**, 2721 (1932).

$\pi \rightarrow \pi^*$ transition shifts hypsochromically with increasing acid concentration, the changes observed occurring at about the same acid concentration as that at which the change in the $n \rightarrow \pi^*$ absorption is observed.

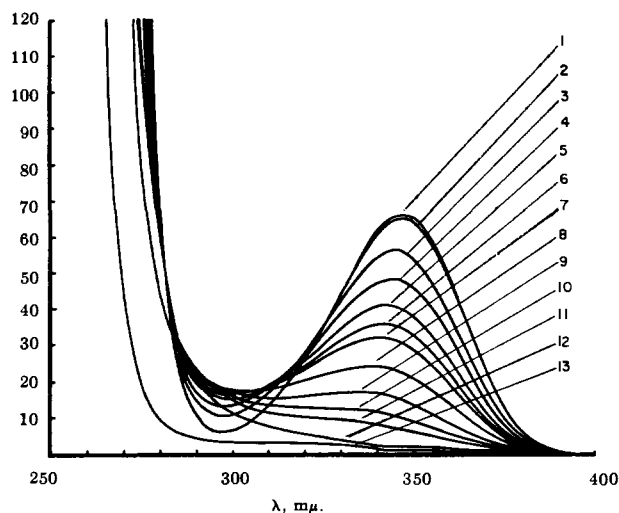


Fig. 3.—Spectra of diisopropyl-N-nitrosamine in aqueous sulfuric acid solutions; the acidity increases from solution 1 to solution 10.

The occurrence of an isoabsorptive point at 275 $m\mu$ suggests that, over the range of acid concentrations where it is found, the system is composed of only two species. However, if the spectral curves of these two species cross more than once, at least one other isoabsorptive point would be expected to be present. Since, with increasing acid concentration, absorption increases in the region of 300 $m\mu$ and decreases in the region near 332 $m\mu$, there is every reason to expect that this system, if composed of two components, will have an isoabsorptive point in the region 300–332 $m\mu$. However, as an isoabsorptive point is *not* observed in this region, it may be concluded that, over the range of acid concentrations where an isoabsorptive point is observed at 275 $m\mu$, the system is composed of at least *three* absorbing species. This concept requires that each of the three species should have the same extinction coefficient at the wave length of the observed isoabsorption point, which is a rare, if not hitherto unobserved, phenomenon. This composition must probably be considered to be a characteristic of the N-nitrosamine system and not due to chance, because the spectra of diisopropyl-N-nitrosamine display comparable behavior. Deviations from the isoabsorptive point at higher acid concentration may be ascribed to the appearance of a *fourth* N-nitrosamine

species, characterized by lack of any distinguishable $n \rightarrow \pi^*$ transition.

The absorption at any wave length of such a system composed of four N-nitrosamine species I–IV, can be represented by

$$EC = E_I C_I + E_{II} C_{II} + E_{III} C_{III} + E_{IV} C_{IV}$$

In this equation of ten variables, C can be predetermined in the preparation of the solutions, E is measured from the spectra, and E_I can be determined from the limiting case where no acid is present and $E = E_I$. A fourth variable is determined by the conservation equation $C = C_I + C_{II} + C_{III} + C_{IV}$. A knowledge of these four variables is, however, insufficient for direct computation of the other variables. Nevertheless, by making certain assumptions and simplifications, it is possible to deduce approximate solutions which are sufficiently accurate to yield considerable insight into the nature of the reactions occurring.

In Fig. 2, curve 1 is the spectrum of dimethyl-N-nitrosamines in neutral solution and therefore represents pure base, I. As the acid concentration is increased, I is displaced by other species having absorption at shorter wave lengths. It may be assumed that the absorption at wave lengths somewhat above that of the maximum (*i.e.*, at about 356 $m\mu$) is due almost entirely to I and, therefore, that the absorption measured at 356 $m\mu$ is a suitable measure of C_I at all but the highest concentrations of acid.

If it be assumed that curve 10 represents pure IV, curve 9 will then represent a mixture of moieties predominantly III and IV and as the absorptivity of IV is small in comparison to that of III, the difference between curves 9 and 10 will principally indicate the disappearance of III and provide an approximation of the shape of the spectral absorption curve of pure III. By multiplying this curve by a suitable constant such that the curve passes through the isoabsorptive point, a curve is obtained which is an approximation of the actual spectrum of pure III (*cf.* Fig. 4 and 5).

If the equilibrium represented by $I + II + III + IV$ could be so limited that only I and II were present, a second isoabsorptive point would then be observed. This condition is approximated when the acid concentration is very low; consequently, the position of the isoabsorptive point of I and II can be estimated to occur at 322 $m\mu$. Because the absorption of III and IV at 322 $m\mu$ must be very low, the absorptivity at 322 $m\mu$ is largely due to I and II, and may be considered to be a measure of $(C_I + C_{II})$.

At the isoabsorptive point at 275 $m\mu$, $E_I = E_{II} = E_{III}$. Hence, $EC = E_I(C_I + C_{II} + C_{III}) + E_{IV}C_{IV}$.

TABLE II

CALCULATED CONCENTRATIONS AND EQUILIBRIUM CONSTANTS OF DIISOPROPYL-N-NITROSAMINE SPECIES IN AQUEOUS SULFURIC ACID SOLUTIONS

Soln.	C_I	C_{II}	C_{III}	C_{IV}	$[H_2SO_4], M$	α_{H^+}	$K_1 =$	$K_1 =$	$K_2 =$	$K_2 =$
							$\frac{C_{II}}{C_I \alpha_{H^+}}$	$\frac{C_{II}}{C_I [H_2SO_4]}$	$\frac{C_{III}}{C_{II} \alpha_{H^+}}$	$\frac{C_{III}}{C_{II} [H_2SO_4]}$
1	0.03075	0	0	0	0	10^{-7}
2	0.0304	0.00035	0	0	0.06	0.186	0.0618	0.192
3	.0236	.00686	0.00021	0	.66	0.457	.636	.461	0.0933	0.064
4	.0193	.00890	.00255	0	.97	1.48	.312	.476	.193	.295
5	.01528	.01047	.00490	0	1.40	4.79	.142	.487	.1024	.334
6	.01288	.01082	.00705	0	1.80	9.13	.0912	.467	.0714	.362
7	.01109	.01096	.00870	0	2.29	17.8	.0555	.431	.0446	.347
8	.00769	.01040	.01265	0	2.75	45.7	.0296	.492	.0269	.442
9	.00465	.00895	.01715	0	3.25	85.1	.0226	.593	.0225	.589
10	.00286	.00748	.02041	0	3.78	132	.0198	.691	.0214	.722
11	.00200	.00400	.02275	0	4.33	309	.00647	.462	.0184	1.314
12	.00107	.00220	.02371	0.00377	6.45	2144	.00096	.319	.00353	1.67
13	.00025	.00179	.00204	0.03075	18.0	10^{10}

By combining this equation with $C = C_I + C_{II} + C_{III} + C_{IV}$

$$C_{IV} = \frac{EC - E_I C}{E_{IV} - E_I}$$

and, by linear combinations of the values previously determined for C_I , $(C_I + C_{II})$, C_{IV} , and C , values of C_{II} and C_{III} at each acid concentration may be obtained.

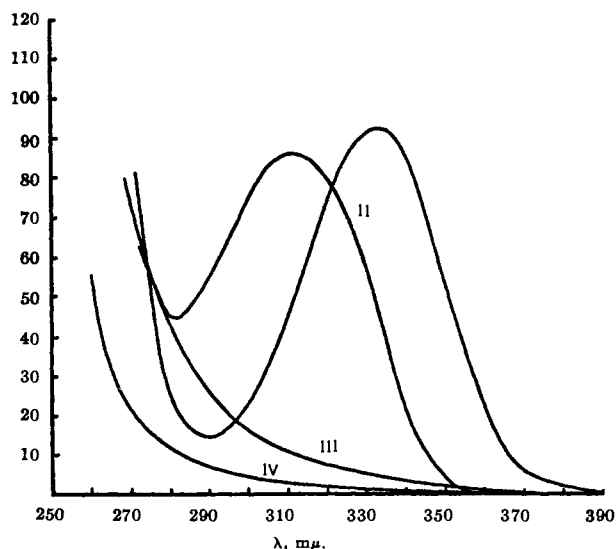


Fig. 4.—Calculated spectra of absorbing species of dimethyl-N-nitrosamine in aqueous sulfuric acid solutions.

Tables I and II summarize the results obtained by this treatment of the spectra shown in Fig. 2 and 3, and list the calculated values of the equilibrium constants for several assumed equilibria. When K_1 is assumed to be $C_{II}/C_I \alpha_{H^+}$, the calculated values of K_1 change greatly and continuously with changing acid concentration, and it is apparent that the equilibrium cannot be represented as a simple function of hydrogen ion activity.

On the other hand, when the equilibrium is regarded as a simple function of molar concentration of acid, a fairly constant set of values of K_1 is obtained. Over the range of acid concentrations employed, the hydrogen ion activity changes to a much greater extent than the molar acid concentration; indeed, the change is so great that the degree of constancy of the equilibrium constant calculated clearly demonstrates that the equilibrium is not to be represented as a simple function of hydrogen ion activity, but as a function of molar acid concentration. The mathematical treatment used employed assumptions which limit the quantitative ac-

curacy of the results obtained; therefore, the data do not unequivocally establish the formulation of the equilibrium constant as $K_1 = C_{II}/(C_I [H_2SO_4])$, yet the extent of agreement, together with the simplicity of the function, makes it appear to be the most probable expression of the equilibrium.

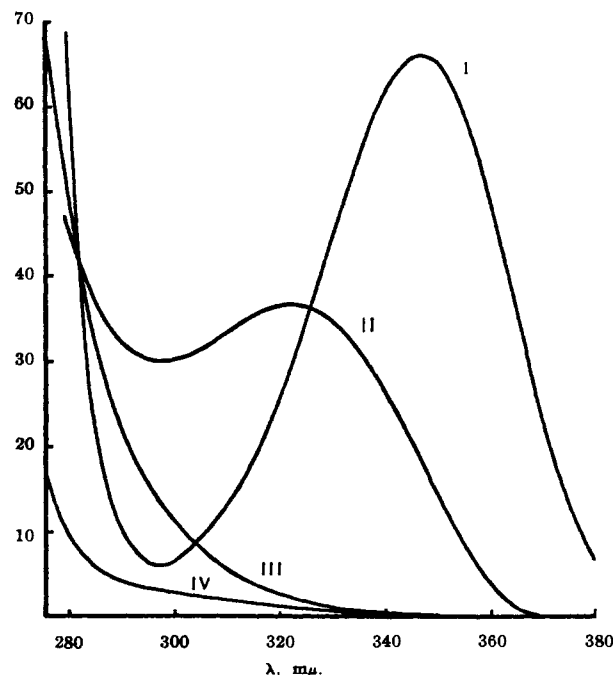


Fig. 5.—Calculated spectra of absorbing species of diisopropyl-N-nitrosamine in aqueous sulfuric acid solutions.

Examination of the spectra gives further evidence of the nature of the species formed. The spectrum of the second N-nitrosamine species II (see Fig. 4 and 5) bears great resemblance to that of the aqueous base itself, which is an indication that II bears strong structural similarity to the base I in aqueous solution. The difference of frequency of maxima of I and II can be equated to an energy difference, which is 5.8 and 5.6 kcal./mole for dimethyl-N-nitrosamine and diisopropyl-N-nitrosamine, respectively; values appropriate to a hydrogen-bonding reaction, but not to a protonation reaction. This evidence, together with that presented concerning the dependence of the equilibrium constant, indicates that the first step of the reaction is the formation of a hydrogen bond.

The nature of the acid species which forms the hydrogen bond is not certain. It may well be molecular

sulfuric acid or bisulfate ion. In any case, spectral change does not occur until acid concentration is increased to a value such that the hydrogen ion activity coefficient becomes greater than unity, and consequently, all of the acid has not dissociated into hydronium ions. It seems probable, therefore, that over the range of acid concentrations where spectral change occurs, free sulfuric acid and bisulfate ion are present, and are presumably available for hydrogen bonding.

For dimethyl-N-nitrosamine, examination of the possible formulations of the *second equilibrium constant* does not distinguish clearly between a dependence of the equilibrium on (a) the molar acid concentration or (b) hydrogen ion activity. However, for diisopropyl-N-nitrosamine, dependence of the equilibrium on molar acid concentration seems indicated. The data for diisopropyl-N-nitrosamine are believed to be more reliable than those for dimethyl-N-nitrosamine; therefore, the demonstrated formulation of K_2 for the former is considered to be more significant than for the latter. Consequently, the most probable formulation of the second equilibrium constant appears to be $K_2 = C_{III}/(C_{II}[H_2SO_4])$. The spectral evidence, *i.e.*, the apparent complete absence of the $n \rightarrow \pi^*$ transition in species III suggests that this species represents a conjugate acid and hence that the second equilibrium is a true acid-base reaction. However, such an equilibrium is not in accord with the foregoing formulation of the equilibrium constant K_2 . It is possible, of course, that the second equilibrium constant may not be accurately represented. On the other hand, representation of the second equilibrium as essentially a solvation reaction presupposes that an $n \rightarrow \pi^*$ transition should occur in the region 260–310 $m\mu$. No such maximum is observed; indeed, it would not be expected to be observable since it would lie in the region of the shoulder of the much stronger $\pi \rightarrow \pi^*$ transition, which should thoroughly mask the much weaker $n \rightarrow \pi^*$ transition.

The data obtained are insufficient even to attempt an evaluation of the equilibrium constant of the third equilibrium.

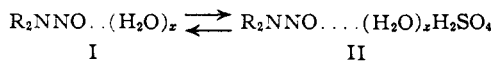
The values given in Table III as best values for the equilibrium constants are obtained as the simple averages of the values indicated by braces in the respective tables.

TABLE III

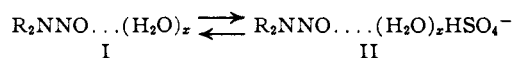
EQUILIBRIUM CONSTANTS OF N-NITROSAMINES IN AQUEOUS SULFURIC ACID SOLUTIONS

N-Nitrosamine	K_1	K_2
Dimethyl-	0.18	0.24
Diisopropyl-	0.47	0.36

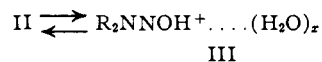
In summary, then, it appears that the first equilibrium observed is represented by



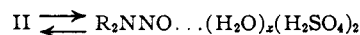
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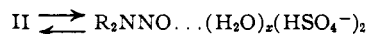
The second equilibrium might be formulated as



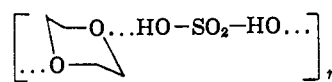
or



or



although further complexing with sulfuric acid or bisulfate seems possible. The last equilibrium most likely involves a true acid-base reaction, either from neutral or monpositive III to the mono- or dipositive IV. On the other hand, another Lewis base, *p*-dioxane, has been demonstrated by X-ray crystallographic determination to form infinite hydrogen-bonded chains with sulfuric acid (V).⁸ It seems possible that one of the N-nitrosamines species belong to such a structure also.



V

N-Nitrosamine-Acid Addition Compounds.—Assuming, as was done above, that some of the equilibria observed involve the actual formation of a conjugate acid, it might be possible to isolate its salts. Since no such salts have ever been reported, it appeared of interest to attempt their preparation and characterization. This was done by mixing the pure N-nitrosamine and concentrated sulfuric acid and observing the mixture for any sign of a chemical reaction. All of the N-nitrosamines available were employed, including all the normal dialkyl-N-nitrosamines through the di-*n*-octyl, several branched-chain compounds and several cyclic N-nitrosamines. In no case was any compound precipitated, and the only evidence of a reaction was generation of some heat and loss of color of the reaction mixture.

The reaction was repeated using 70% aqueous perchloric acid, whereupon white, crystalline precipitates were obtained within seconds from di-*n*-heptyl-N-nitrosamine and bis-(2-ethylhexyl)-N-nitrosamine. These precipitates were filtered off and dried on a porous porcelain plate but could not be completely freed from solvent owing to the low vapor pressure of perchloric acid solutions. The crystals slowly decomposed when the temperature was raised above 30°. The crystals are highly soluble in polar solvents, slightly soluble in benzene, insoluble in ether and hexane, and could not be recrystallized. Titration of a weighed portion of crude crystals prepared from di-*n*-octyl-N-nitrosamine in aqueous solution suggested that their composition corresponded to a 1:1 molar combination of the N-nitrosamines and perchloric acid.

(8) O. Hassel and C. Romming, *Acta Chem. Scand.*, **14**, 398 (1960).