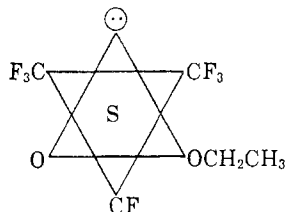


contains stereochemically non-equivalent CF_2 groups. This may be explained by assuming a substituted ethane-type structure²⁰ in which the non-equivalence arises from a



(20) J. A. Pople, *Mol. Phys.*, **1**, 1 (1958).

time averaging process of energetically different rotational isomers.

At room temperature there are two resonances of approximate relative intensities six and one assignable to CF_2 and CF fluorine atoms (Fig. 1f). At -20° , the CF_2 resonance is resolved into two separate resonances. Divergence of these resonances continues to -100° , at which temperature the sample begins to form a glass. Each CF_2 resonance consists of a quintuplet structure. Although eight-line patterns are expected, quintuplet structures are observed as a result of overlap of peaks arising from nearly equivalent CF_2 - CF_2 and CF_2 - CF spin coupling.

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Amine-Sulfur Dioxide Complexes. Solid-Liquid-Gas Equilibria and Infrared Spectra of Complexes with N,N-Dimethylanilines

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Sulfur dioxide has been found to form 1:1 addition compounds with N,N-dimethyl-*o*-toluidine, N,N-dimethyl-*m*-toluidine, and N,N-dimethyl-*p*-toluidine. In contrast to the *meta* and *para* derivatives and the previously reported complex of SO_2 with N,N-dimethylaniline, the *ortho* complex is highly unstable. Solid-liquid-gas equilibrium pressures have been measured at several temperatures for the *meta* and *para* compounds and for N,N-dimethylaniline- SO_2 . From the resulting data ΔH° , ΔF° , and ΔS° for the decomposition of the solid complexes have been computed. The infrared spectra of all four complexes have been obtained in the liquid state and may be interpreted as providing evidence for the charge-transfer nature of these materials. The infrared data, together with the generally high stability of the complexes, are consistent with binding of SO_2 at the amine nitrogen. This idea is supported by the 1:2 mole ratio found for the previously unreported N,N,N',N'-tetramethyl-*p*-phenylenediamine- SO_2 . It is suggested that the low stability of N,N-dimethyl-*o*-toluidine- SO_2 may be due primarily to shielding of the nitrogen by the *ortho* methyl group.

Introduction

Complexes of amines with sulfur dioxide have long been known¹; however, there are important gaps in information on the general properties of these materials, and almost no attention has been given to their structures. A study of properties and structures of such complexes therefore has been initiated in this Laboratory. Of particular interest is the possible application of the Mulliken charge-transfer theory.²⁻⁴

Although the SO_2 complexes of aniline,⁵ and *o*-

m-, and *p*-toluidine⁶ are known, the only known SO_2 complexes with the N-substituted aromatic amines include those with N-methylaniline, N-ethylaniline,⁷ and N,N-dimethylaniline.^{8,9} In the current study the SO_2 complexes of N,N-dimethylaniline and N,N-dimethyl-*o*-, *m*-, and *p*-toluidines have been examined along with the SO_2 complex of N,N,N',N'-tetramethyl-*p*-phenylenediamine.

An important question relative to these SO_2 addition compounds is the site of the base- SO_2 linkage. It is not clear as yet whether the SO_2 is bound to the amine nitrogen or to the π -electron system of the ring. The related question of steric hindrance is likewise of interest. Tsubomura⁹ found evi-

(1) A critical review of much of the early work has been given by A. E. Hill, *J. Am. Chem. Soc.*, **53**, 2598 (1931). The earliest reference on these materials is A. W. Hoffman, *Ann. Chem. Pharm.*, **47**, 64 (1843).

(2) R. S. Mulliken, *J. Am. Chem. Soc.*, **72**, 600 (1950).

(3) R. S. Mulliken, *ibid.*, **74**, 811 (1952).

(4) R. S. Mulliken, *J. Phys. Chem.*, **56**, 801 (1952).

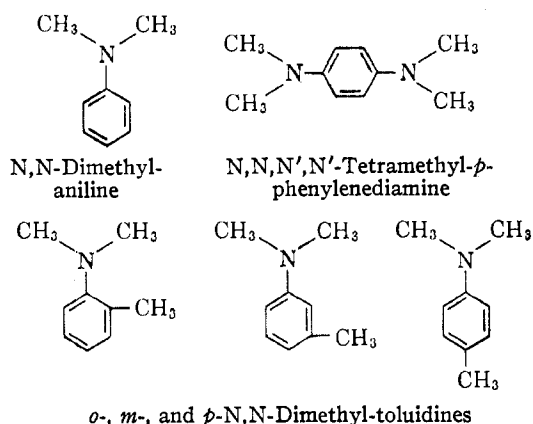
(5) A. E. Hill, *J. Am. Chem. Soc.*, **53**, 2598 (1931).

(6) A. E. Hill and T. B. Fitzgerald, *ibid.*, **57**, 250 (1935).

(7) H. W. Foote and J. Fleischer, *ibid.*, **56**, 870 (1934).

(8) J. R. Bright and W. C. Fernelius, *ibid.*, **65**, 637 (1943).

(9) H. Tsubomura, *ibid.*, **32**, 40 (1960).



dence that in complexes of N,N-dimethylanilines with iodine, binding is mainly at the amine nitrogen, classifying⁴ the amines essentially as n-(or onium) donors, and that *ortho* substituents reduce markedly the strength of the complex.

Only one investigation of the structure of an SO₂-aniline complex seems to have been reported. Bright and Jasper,¹⁰ from a study of the parachor of N,N-dimethylaniline-SO₂, suggested that an N-O linkage is involved. The postulate merits examination.¹¹

Experimental

Materials.—N,N-dimethylaniline and its *o*-, *m*-, and *p*-methyl derivatives were Eastman White Label materials. All were fractionally distilled from zinc dust and stored in the dark under wax seal until used. Boiling points (pressure 78 mm.) and refractive indices of the fractions used were: N,N-dimethyl-*o*-toluidine, 105°, n_D^{20} 1.5252 (lit.¹² 1.5255); *meta*, 125–126°, n_D^{20} 1.5488 (lit.¹² 1.5492); and *para*, 129–130°, n_D^{20} 1.5466 (lit.¹² 1.54603). N,N-dimethylaniline, similarly distilled, had n_D^{20} 1.5558 (lit.¹³ 1.5556). Normal boiling points¹⁴ are *ortho*, 184.6°; *meta*, 212.5°; *para*, 210–211°; and N,N-dimethylaniline, 192.5–193.5°. The infrared spectra of these materials showed at most only barely detectable traces of moisture.

N,N,N',N'-tetramethyl-*p*-phenylenediamine was prepared from the Eastman White Label dihydrochloride by adding 10% by weight NaOH until the mixture was basic to litmus. The amine suspension was extracted with portions of ether approximately equal in volume to the aqueous phase, until the latter was clear. After the ether had evaporated in air, the crude product was recrystallized from aqueous ethanol, and allowed to dry in air. The m.p. was 50–51° (lit.¹⁴ 51°).

Sulfur dioxide, Matheson anhydrous grade, stated minimum purity 99.98%, was bubbled through concentrated H₂SO₄ before being used.

(10) J. R. Bright and J. J. Jasper, *J. Am. Chem. Soc.*, **63**, 3486 (1941).

(11) G. Cilento, *Chem. Rev.*, **60**, 147 (1960).

(12) H. Ley and G. Pfeiffer, *Ber.*, **54B**, 368 (1921).

(13) A. E. Comyns, *J. Chem. Soc.*, 1557 (1955).

(14) C. D. Hodgman, ed., "Handbook of Chemistry and Physics," 43rd Ed., Chemical Rubber Publishing Co., Cleveland, Ohio, 1961.

CCl₄, Fisher Certified "Spectranalyzed Reagent," was used as received.

Preparation of Complexes. (a) **General Procedure.**—Complexes usually were prepared in a Pyrex flask made by sealing an inner ground glass connection to a 50-ml. erlenmeyer flask.

A modified Foote and Fleischer⁷ method was used. In the latter, excess SO₂ was condensed on weighed amine (1–2 ml. in these experiments) at –20°, and the excess vaporized through a mercury trap at a temperature where the solution vapor pressure, but not that of the complex, exceeds 1 atm. The weight increase (corrected for air displacement by SO₂) yields the product composition.

Care was taken at all times to protect reagents and products from moisture. Standard vacuum line procedures were used.

(b) **N,N-Dimethyl-*p*-toluidine-SO₂.**—This 1:1 complex was prepared as above, excess SO₂ being removed, to the extent possible, at room temperature. Since the complex is highly soluble in SO₂, crystallization from SO₂ was difficult unless the SO₂ pressure above the solid at –20° was reduced by exposing the system to the vacuum pump.

The product at –20° consists of light yellow needles. On slow warming in an evacuated system it darkens with gradual increase in pressure and, at about 31°, is slightly decomposed as indicated by the appearance of droplets of orange-red liquid. The SO₂ odor of the material at room temperature is further indication of decomposition. The linearity of log *P* vs. 1/*T* for the solid-liquid-gas equilibrium (Table I) is consistent with the presence of a single solid phase. Like N,N-dimethylaniline-SO₂,¹⁰ the complex, protected from moisture, may be stored in a stoppered container at room temperature. The 1:1 complex picks up SO₂ under an SO₂ pressure of 1 atm. to give a solvate which is liquid at 36°.

Synthesis ratio: 5.728 mmoles of amine combined with 5.727 mmoles of SO₂.

(c) **N,N-Dimethyl-*m*-toluidine-SO₂.**—This 1:1 complex was prepared as above, excess SO₂ being removed, to the extent possible, at 0°. At –20° it is a light yellow solid, highly soluble in liquid SO₂. At room temperature it is a red liquid, smelling strongly of SO₂, which can be stored as described above. Again, the linearity of log *P* vs. 1/*T* (Table I) is consistent with the presence of a single solid phase. The 1:1 complex picks up SO₂ under an SO₂ pressure of 1 atm. to give a solvate which is liquid at 22°.

Synthesis ratio: 5.692 mmoles of amine combined with 5.535 mmoles of SO₂.

(d) **N,N-Dimethylaniline-SO₂.**—A 1:1 mole ratio and a m.p. of 12.6° have been reported for this material, a red oil at room temperature.⁸ Attempts to prepare the solid form as above were unsuccessful; the following procedure was used. After adding excess SO₂ to the amine, the sample was connected to the vacuum line and the SO₂ pressure adjusted to about 300 mm. at 25°, which is somewhat greater than the equilibrium SO₂ pressure in the 1:1 liquid.⁸ When cooled to –70°, the sample crystallized immediately. Excess SO₂ was pumped out at –20°. The product, yellow to orange needles, is extremely soluble in SO₂.

Synthesis ratio: 5.631 mmoles of amine combined with 5.698 mmoles of SO₂.

TABLE I
THERMODYNAMIC FUNCTIONS FOR THE DECOMPOSITION OF SOLID COMPLEXES
OF SULFUR DIOXIDE WITH N,N-DIMETHYLANILINES

Compound	Amine pK _a in 50% alcohol ^a	Amine I (e.v.)	SO ₂ pressure equation ^b		$\Delta F_{298.16}^{\circ}$ (cal./ mole)	ΔH (kcal./ mole)	$\Delta S_{298.16}^{\circ}$ (e.u.)
			A	B			
N,N-Dimethylaniline-SO ₂	4.21	ca. 7.3 ^{d,e}	2531	10,576	(1082) ^c	11.6	(35.2) ^c
N,N-Dimethyl- <i>m</i> - toluidine-SO ₂	4.66	...	4674	17,707	(1159) ^c	21.4	(67.8) ^c
N,N-Dimethyl- <i>p</i> - toluidine-SO ₂	4.94	ca. 7.0 ^d	5059	18,333	2067	23.1	70.7
N,N-Dimethyl- <i>o</i> - toluidine-SO ₂	5.51	ca. 7.5 ^d					

^a H. C. Brown, D. H. McDaniel, and O. Häfiger in E. A. Braude and F. C. Nachod, "Determination of Organic Structures by Physical Methods," Academic Press, Inc., New York, N. Y., 1955, p. 596. ^b Constants for equation $\log P_{\text{mm}} = (-A/T) + B$ for pressure of SO₂ above 1:1 complex. ^c Theoretical; computed from theoretical value for $P_{298.00}$. ^d J. R. Platt (as reported by H. Tsubomura and R. S. Mulliken, *J. Am. Chem. Soc.*, **82**, 5966 (1960)). ^e G. Briegleb and J. Czekała, *Z. Elektrochem.*, **63**, 6 (1959).

(e) **N,N-Dimethyl-*o*-toluidine-SO₂**.—When excess SO₂ was condensed on the amine at -20° , and the excess boiled off at room temperature and 1 atm., an orange-red 1:1 liquid complex remained. It could not be crystallized when evacuated cautiously either at -70 or -20° . In contrast to the SO₂ complexes described above, it is highly unstable; at room temperature in an open container it loses SO₂ rapidly, leaving only the colorless amine.

Synthesis ratio: 6.027 mmoles of amine combined with 5.835 mmoles of SO₂.

(f) **N,N,N',N'-Tetramethyl-*p*-phenylenediamine-2SO₂**.—When treated with excess SO₂ at -20° , and the excess removed at room temperature, the amine gave an orange-red 1:2 solid which was insoluble in SO₂. Its m.p. in a sealed capillary was $91-93^{\circ}$. In air it lost its color only slowly.

Synthesis ratio: 0.6362 mmole of amine combined with 1.215 mmoles of SO₂.

(g) **Secondary Reaction Products**.—To determine if secondary products accompany complex formation between SO₂ and N,N-dimethylaniline, SO₂ was completely removed from the complexes by evacuation, and the residue examined by infrared spectroscopy. Even with a sample which had set for several weeks at temperatures up to 27° , the N,N-dimethylaniline was recovered unchanged. This is in marked contrast to SO₂-primary amine systems¹⁵ and the reported action of iodine on N,N-dimethylanilines.^{9,16,17}

Equilibrium Pressures.—To determine equilibrium pressures, the flask containing the analyzed sample was attached to the vacuum line, cooled to -20° , and evacuated. The coolant was replaced by a constant temperature water bath, and pressures were measured at intervals until they were constant. A stopcock immediately above

the sample was then closed, and the upper portion of the system partially evacuated. On reopening the stopcock, pressure measurements were continued until the values again were steady. This procedure was repeated until two successive evacuations gave stable pressures which agreed within the precision limits of the measurements. Measurements then were taken at other temperatures and could be verified as above. In some cases, especially at low temperatures, it was necessary, after partial evacuation, to heat the system to a higher temperature before the equilibrium pressure could be reproduced.

The thermometer had been standardized against one calibrated by the National Bureau of Standards. Temperature control was $\pm 0.1^{\circ}$ or better.

Manometer differences were determined with a cathetometer and always were accompanied by a barometer reading. Both measurements were corrected to 0° before computing the pressures.

Because the sample was spread thinly and had a large surface, equilibrium was quickly attained, usually within 20 min. after a partial evacuation or a resetting of the temperature. Equilibrium pressures were reproducible to ± 0.5 mm.

Infrared Spectra.—Spectra were recorded on a Perkin-Elmer Infracord spectrophotometer equipped with NaCl optics. Polystyrene was the calibration standard. Primary attention was given the region $1400-1100$ cm.⁻¹.

The spectra of all complexes except N,N-dimethyl-*o*-toluidine-SO₂ were taken on liquid films of mixtures of SO₂ in the amine, sandwiched between two rock salt plates. At least two different samples of each complex were examined. Some of the N,N-dimethylaniline-SO₂ samples were prepared by the method of Bright and Fernelius.⁸ Each sample used gave a reproducible spectrum.

With the unstable N,N-dimethyl-*o*-toluidine-SO₂, the 1:1 liquid was quickly introduced between two rock salt plates separated by a 0.025 mm. lead spacer. The assembly was placed immediately in a demountable cell holder, and the cover of the latter firmly secured. Reproducible spectra were easily obtained.

For comparison, the spectra of SO₂ (saturated solution in CCl₄) and of the free amines were taken. The amine

(15) Unpublished observations; a more complete report on this phenomenon is planned for a subsequent paper.

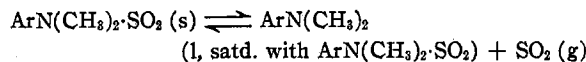
(16) B. Z. Seakowski and G. S. Panson, *J. Org. Chem.*, **26**, 943 (1961).

(17) As expected, systems of SO₂ with N,N-dimethylanilines easily absorb moisture. The products, at room temperature and low SO₂ concentrations, are viscous, almost colorless liquids, which form on the bottom of the container. At higher SO₂ concentrations, the material may crystallize. In excess SO₂ it appears to dissolve completely.

spectra were taken under the same conditions as those of the corresponding complexes.

Results

Equilibrium Pressures and Thermodynamic Constants.—The reaction which occurs when an excess of solid 1:1 complex stands in an evacuated system appears to be



Assuming that the equilibrium constant may be expressed by partial pressures, we have

$$K' = \frac{p_{\text{ArN}(\text{CH}_3)_2} p_{\text{SO}_2}}{p_{\text{ArN}(\text{CH}_3)_2 \cdot \text{SO}_2}}$$

At a given temperature, the partial pressure of amine (saturated with complex) is constant. The same is true of the partial pressure of the complex. Hence, the equilibrium constant may be written as

$$K = p_{\text{SO}_2}$$

Over the temperature range of the measurements, pressures for the pure amines may be computed from available data¹⁸: N,N-dimethylaniline (5.7–9.0°), 0.18–0.24 mm.; N,N-dimethyl-*m*-toluidine (11.9–16.5°), 0.3–0.4 mm.; and N,N-dimethyl-*p*-toluidine (20.0–30.0°), 0.1–0.2 mm. These values, assumed as upper limits for the amine partial pressures in the solid-liquid-gas systems, fall within the precision range of the measurements, and are negligible compared with the measured equilibrium pressures (12.0–44.5 mm.). Partial pressures of the corresponding undissociated complexes should be even smaller. Thus, the total pressure P may be taken as the pressure of SO_2 and hence as the equilibrium constant.

$\log P$ vs. $1/T$ values, treated by the method of least squares, yielded the equations of Table I. Pressures computed therefrom agree with the experimental values to within 0.5 mm. In the case of N,N-dimethylaniline- SO_2 and N,N-dimethyl-*m*-toluidine- SO_2 , the equations have been used to calculate theoretical values of P at 25.0° (a temperature too high for the solid-liquid-gas equilibrium) for use in the thermodynamic calculations.

Thermodynamic constants for the dissociation reactions are summarized in Table I. The ΔH values were obtained from the slopes of the lines as given by the $\log P$ vs. $1/T$ equations.

(18) D. R. Stull, *Ind. Eng. Chem.*, **39**, 517 (1947).

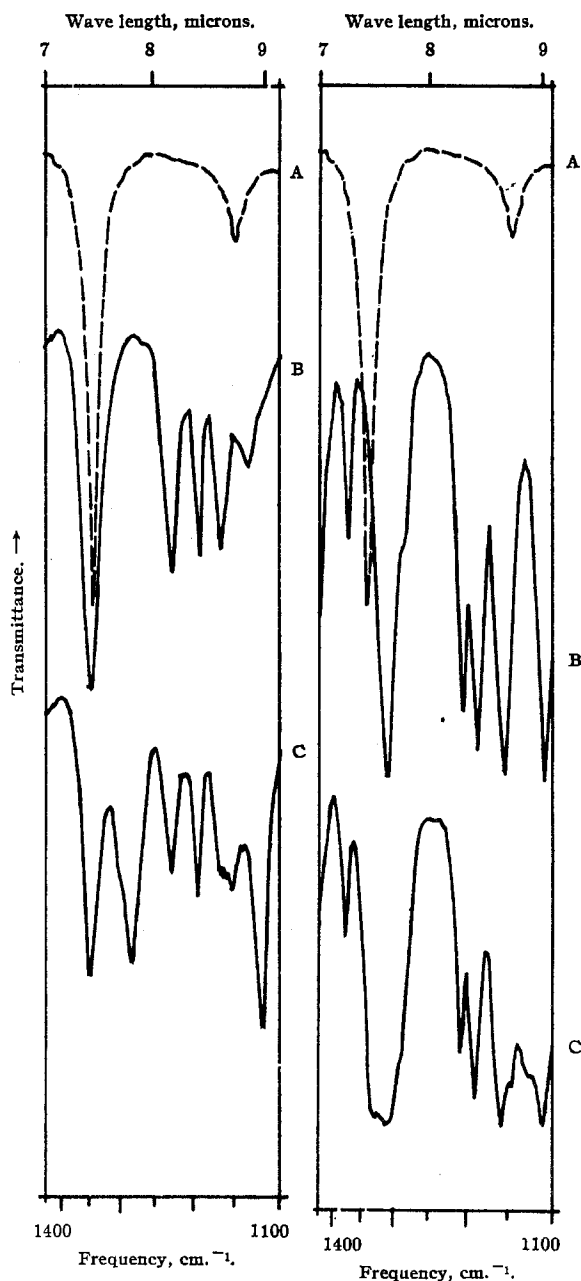


Fig. 1.—Infrared spectra: (A) SO_2 (in CCl_4); (B) N,N-dimethylaniline; (C) N,N-dimethylaniline- SO_2 .

Fig. 2.—Infrared spectra: (A) SO_2 (in CCl_4); (B) N,N-dimethyl-*o*-toluidine; (C) N,N-dimethyl-*o*-toluidine- SO_2 .

Infrared Spectra.—Figure 1 shows spectral changes on complexing in the system N,N-dimethylaniline- SO_2 between 1400 and 1100 cm^{-1} , and is typical of the changes observed also with N,N-dimethyl-*m*-toluidine- SO_2 and N,N-dimethyl-*p*-toluidine- SO_2 .

Figure 2 shows corresponding changes in the system N,N-dimethyl-*o*-toluidine- SO_2 .

Preliminary observations on the spectra of the complexes over the remainder of the rock salt region may be summarized as given below.

N,N-dimethylaniline-SO₂: new bands at (cm.⁻¹) *ca.* 1463 (m), 1047 (w), 936 (m), 763 (s) (shoulder), 735 (m) (shoulder); decrease in intensity of amine bands at *ca.* 1445, 1064, and 948 cm.⁻¹.

N,N-dimethyl-*m*-toluidine-SO₂: new bands at (cm.⁻¹) *ca.* 1463 (m), 1047 (w), 861 (m), 781 (s) (shoulder), and 705 (m) (shoulder); decrease in intensity of amine bands at *ca.* 1445 and 1064 cm.⁻¹, but an increase in intensity of the amine band at 962 cm.⁻¹.

N,N-dimethyl-*p*-toluidine-SO₂: new bands at (cm.⁻¹) *ca.* 1463 (m), 1045 (m), 935 (m), and 819 (s) (the latter apparently a shift in the band found at about 810 cm.⁻¹ in the uncomplexed amine); decrease in intensity of the amine band at *ca.* 1445 cm.⁻¹.

N,N-dimethyl-*o*-toluidine-SO₂: intensity increase in the 939 cm.⁻¹ region.

Finally, in all the complexes except N,N-dimethyl-*o*-toluidine-SO₂ there is some intensity decrease in the 3000 cm.⁻¹ region (C-H stretching vibrations).

Discussion

Table I shows that, excluding the *ortho* compound, the thermodynamic constants for the decomposition reaction (assuming the indicated extrapolations to be valid) increase with increase in amine *pK_a* and apparently also with decrease in amine ionization potential.

Evaluation of the amine-SO₂ bond strengths from the ΔH values is difficult since the latter include crystal lattice energies. However, of the four SO₂-N,N-dimethylanilines, the *ortho* complex is clearly the most unstable.

The great instability of N,N-dimethyl-*o*-toluidine-SO₂ parallels the behavior of complexes between hindered N,N-dimethylanilines and iodine,⁹ trinitrobenzene,¹⁹ and chloranil.²⁰ Equilibrium constants (moles⁻¹ cm.³) for complex formation at 20° in butyl ether were found to be 3.05, 4.09, and 4.03, respectively, for the complexes of chloranil with N,N-dimethylaniline, N,N-dimethyl-*m*-toluidine, and N,N-dimethyl-*p*-toluidine, but only 0.42 for N,N-dimethyl-*o*-toluidine-chloranil.

The ΔH values of the present study are about the same as, or somewhat smaller than, corresponding values for the SO₂ complexes of aniline (19.6 kcal./mole),⁵ *o*-, *m*-, and *p*-toluidine (20.2,

(19) H. Ley, R. Grau, and W. Emmerich, *Ber.*, **58B**, 1765 (1925).

(20) N. H. Smith, Ph.D. Thesis, University of Chicago, 1955.

22.6, and 24.1 kcal./mole, respectively),⁶ and N-methylaniline.²¹

The ΔH of 11.6 kcal./mole for N,N-dimethylaniline-SO₂ seems low in comparison with the ΔH values for the other two complexes, and also when compared with the figure of about 15 kcal./mole found²² for the heat of solution of SO₂ in N,N-dimethylaniline to form the 1:1 *liquid* complex. A possible explanation may be unusually extensive self-association of the liquid amine, released, only slightly above its m.p. (2.5°¹⁴), through breakdown of the 1:1 solid. Such a process, assumed to be exothermic, would reduce the net ΔH of the dissociation reaction; also, it seems consistent with what appear to be relatively high equilibrium pressures for this system.

The similarity of the spectral changes which accompany complex formation and their disappearance on removal of SO₂ are good indications that the changes are characteristic of the complexes and are not due to impurities or stable reaction products. Further, the changes are consistent with what would be predicted by the charge-transfer theory.^{3,23}

According to this theory, an amine-SO₂ complex may be regarded as a resonance hybrid of a no-bond structure D, SO₂ (D = electron donor, the amine) and an ionic structure D⁺-SO₂⁻. The latter is presumed to result from the transfer of an electron from a bonding orbital of the donor to an antibonding orbital of the acceptor, giving a decrease in bond strength, and hence of vibrational frequency, of those bonds whose orbitals are directly involved in the charge-transfer. Further, these effects should be more pronounced the more localized the orbitals concerned.

Information on band assignments for tertiary aromatic amines seems insufficient to justify efforts to explain all the spectral changes. Attention will be confined to the 1400-1100 cm.⁻¹ region, which includes amine and SO₂ vibrations of particular significance for this study.

Assignment of the strong amine bands at 1348 (N,N-dimethylaniline), 1351 (*meta*), 1342 (*para*), and 1316 (*ortho*) to the C-N stretching mode is consistent with the range (1360-1310 cm.⁻¹) re-reported for this vibration²⁴ in tertiary aromatic amines.

(21) A ΔH of about 24 kcal./mole can be computed from the data of Foote and Fleischer (footnote 7) for the N-methylaniline-SO₂ complex.

(22) J. Balej and A. Regner, *Collection Czech. Chem. Commun.*, **21**, 1545 (1956).

(23) R. S. Mulliken, *J. Chem. Phys.*, **23**, 397 (1955).

(24) N. B. Colthup, *J. Opt. Soc. Am.*, **6**, 397 (1950).

Appearance of the asymmetric and symmetric SO_2 stretching bands at 1346 and 1149 cm^{-1} , respectively, is reasonable in view of the lowering of these frequencies (from gas phase values²⁵ of 1361 and 1151 cm^{-1}) observed in the Raman spectrum of CCl_4 solutions.²⁶

The very strong absorption in all four complexes at about 1120 cm^{-1} appears to represent the symmetric stretching vibration shifted from 1149 cm^{-1} (in CCl_4). The striking increase in its relative intensity seems to parallel observations on the acceptor spectra of other complexes.^{27,28}

With *N,N*-dimethyl-*o*-toluidine- SO_2 , the C-N stretching frequency appears at 1299 cm^{-1} as a shoulder on the undisplaced band (1316 cm^{-1}) while the asymmetric S-O stretching frequency is shifted from 1346 cm^{-1} (in CCl_4) to 1325 cm^{-1} . The greater intensity of the displaced S-O band compared with the displaced C-N band has been made use of in assigning bands of the other complexes.

In the spectra of *N,N*-dimethylaniline- SO_2 , *N,N*-dimethyl-*m*-toluidine- SO_2 , and *N,N*-dimethyl-*p*-toluidine- SO_2 , new bands appear at about 1280 and 1299 cm^{-1} (shoulder on the 1280 cm^{-1} band). It seems reasonable that one of these is the displaced S-O stretching frequency and the other the displaced C-N stretching frequency. On the basis of the relative intensities of the corresponding bands in *N,N*-dimethyl-*o*-toluidine- SO_2 , we suggest that the intense 1280 cm^{-1} band is due to the S-O vibration, and the less intense shoulder to the C-N motion.

The spectral changes on complexing are approximately the same in all the materials except that they are considerably less pronounced in the highly unstable *N,N*-dimethyl-*o*-toluidine- SO_2 . This agrees with expectations from the charge-transfer theory and is consistent with observations on other systems.²⁷⁻²⁹

Perhaps the most impressive feature of the spectra is the decrease in frequency of the C-N stretching vibration and the decrease in intensity of the undisplaced band. This may indicate binding of SO_2 at the nitrogen.

It is of interest that a decrease in C-N frequency is observed even with the weak *N,N*-dimethyl-*o*-

(25) G. Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules," D. Van Nostrand Co., New York, N. Y., 1945, p. 285.

(26) H. Gerding and W. J. Nijveld, *Rec. trav. chim.*, **56**, 968 (1937).

(27) W. B. Person, R. E. Humphrey, W. A. Deskin, and A. I. Popov, *J. Am. Chem. Soc.*, **80**, 2049 (1958).

(28) W. B. Person, R. E. Humphrey, and A. I. Popov, *ibid.*, **81**, 273 (1959).

(29) E. K. Plyler and R. S. Mulliken, *ibid.*, **81**, 823 (1959).

toluidine- SO_2 . This may be evidence that the amine, though sterically hindered, is still primarily an n-donor toward SO_2 . In such a case, since the $\text{p}K_a$ of the amine is so high, the instability of its SO_2 complex could be due principally to steric shielding of the nitrogen by the *ortho* methyl group.

The striking nature of the spectral changes on complexing also may indicate binding at the nitrogen. In the infrared spectra of complexes of certain π -donors (olefins and substituted benzenes) with sulfur dioxide, Booth, Dainton, and Ivin³⁰ found no splitting of S-O frequencies, and only minor changes generally in the spectra of the donors. However, Tramer³¹ found conspicuous changes in the vibrational (Raman) spectrum of the pyridine- SO_2 complex, where the amine appears to act as an n-donor.

If binding is at the nitrogen, one would predict 1:2 diamine- SO_2 complexes, provided the two nitrogens are far enough apart to prevent mutual interference of the sulfur dioxide molecules. This prediction is verified in the case of the *N,N,N',N'*-tetramethyl-*p*-phenylenediamine- 2SO_2 complex.

Tsubomura,⁹ from an examination of the donor properties of *N,N*-dimethylaniline by the molecular orbital theory, has postulated that donor action probably is essentially at the nitrogen atom. His experimental study⁹ of the stabilities of complexes of iodine with *N,N*-dimethylanilines, and the results here reported on SO_2 complexes, appear to support this idea.

If the lowest unoccupied orbital of sulfur dioxide is antibonding and localized mainly on the sulfur atom,³² and if one assumes that in *N,N*-dimethylaniline- SO_2 complexes electron transfer occurs from an orbital localized mainly on the nitrogen to the acceptor orbital of lowest energy,²³ the result would appear to be essentially a nitrogen-sulfur bond.

The possible existence of isomeric complexes in systems such as these has been pointed out.³³ As mentioned previously, the linearity of the log P vs. $1/T$ data is consistent with the presence of only one solid complex under the conditions of the measurements. Present data seem insufficient to determine if isomeric liquid complexes are present. We hope to investigate this point further.

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Reactions of Nitrogen(II) Oxide with Miscellaneous Lewis Bases

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Our previous studies of reactions of nitrogen(II) oxide with primary and secondary amines have been extended to reactions of trimethylamine, diamines, aromatic and aliphatic sulfides and thiols, phosphines, phosphites, triphenylarsine, triphenylstibine, and sodium phenoxide. N_2O_2 adducts are formed with the amines. In the presence of strong bases, mercaptans are converted to disulfides in good yields. Triphenylphosphine and triethylphosphite were converted to the phosphine oxide and phosphate, respectively. Starting materials were recovered when reaction was attempted under the reported conditions with triphenylarsine, triphenylstibine, dialkyl sulfides, thiophene, or sodium phenoxide.

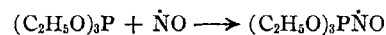
Introduction

The reaction of nitric oxide with sulfite ion² and with various primary and secondary amines^{3,4} produces: $SO_3N_2O_2^{-2}$, $RNH_3^+RNHN_2O_2^-$, and $R_2NH_2^+R_2NN_2O_2^-$, respectively. It was of interest to study the reaction of nitrogen(II) oxide with tertiary amines, diamines, and other group V and VI donors.

Trimethylamine on reaction with nitric oxide gives rise to the very unstable product $(CH_3)_3NN_2O_2$. Solids of moderate stability are isolated from the reaction of piperazine and N,N' -dimethylethylenediamine with nitric oxide.

In studies of sulfur and phosphorus donors as well as triphenylarsine, triphenylstibine, and sodium phenoxide, we were not able to isolate products containing nitrogen. In cases where reaction occurs, products arising from the "oxidizing" nature of nitric oxide are produced. Aliphatic and aromatic mercaptans in the presence of sodium methoxide produce disulfides, whereas triphenylphosphine is converted to triphenylphosphine oxide and triethylphosphite to triethylphosphate. Some of the above oxidations are convenient synthetic procedures that

yield products of high purity directly. The kinetics for the reaction of nitric oxide with triethylphosphite have been studied.⁵ The results indicate that the first step is rate controlling and is represented by the equation



Experimental

Purification of Materials.—Matheson commercial grade nitric oxide may be used directly. Eastman Kodak or Pitt-Consol freshly distilled liquids or dry recrystallized solids were used as starting materials. Triethylphosphite was distilled from anhydrous BaO.

Instrumentation.—Infrared spectra were obtained with a Perkin-Elmer Model 21 infrared spectrophotometer with sodium chloride optics. The instrument was frequency calibrated using the absorptions of ammonia, water vapor, and polystyrene, and the appropriate corrections were applied to the spectral data reported.

General Procedure for Sulfur Compounds.—Equimolar quantities of mercaptan and freshly prepared sodium methoxide are dissolved in methanol, placed in an air-tight three-neck flask, and cooled to ice bath temperature. The procedure employed is that previously described³ as the atmospheric pressure method. The products are either white or light yellow solids which precipitate from solution after 20 to 30 min., or clear light yellow liquids which are distilled from the reaction mixture. The solids are conveniently recrystallized from methanol or hexane. Products obtained from the corresponding mercaptans are listed in Table I. Boiling points, melting points, and spectra agree with reported data.

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