

ion, which seems to be very weak due to lack of vibrational perturbation, but to appear through a solvent perturbation.¹⁶ In that case also, the band is found to be much stronger in the hydroxylic solvents.

In the sodium nitrite crystal, band II is found to be weak and x -polarized,⁶ which would be the case for a band of this type which was perturbed by the b_2 vibration. Thus the most reasonable assignment for band II seems to be as the $n_O \rightarrow \pi^*$ transition of symmetry ${}^1A_2 \leftarrow {}^1A_1$.

Summary

We have presented data on the effects of different solvents on the near-ultraviolet electronic spectrum of nitrite ion. A consideration of the frequency shifts and

(16) S. J. Strickler and M. Kasha, to be published.

intensities of the three bands provides evidence of the nature of the transitions and the orbitals involved.

The results we have obtained are in good agreement with the polarization data in crystalline sodium nitrite^{5,6} and with the results of quantitative theoretical calculations.¹³ Because of this, we believe that the assignment of the three bands may be made with confidence as: Band I (near 3600 Å.) is an $n \rightarrow \pi^*$ transition of symmetry ${}^1B_1 \leftarrow {}^1A_1$, where the nonbonding orbital is predominantly on the oxygen atoms. Band II (near 2800 Å.) is an $n_O \rightarrow \pi^*$ transition of electronic symmetry ${}^1A_2 \leftarrow {}^1A_1$. Band III (near 2100 Å.) is a $\pi \rightarrow \pi^*$ transition of symmetry ${}^1B_2 \leftarrow {}^1A_1$. In addition, the onset of a fourth band is observed at still higher energies in acetonitrile solution, and it is suggested that this is an "electron transfer" band.

[CONTRIBUTION FROM THE FUELS AND LUBRICANTS DEPARTMENT, GENERAL MOTORS RESEARCH LABORATORIES, WARREN, MICH.]

The Atmospheric Thermal Oxidation of Nitric Oxide¹

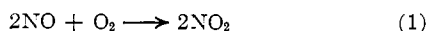
BY WILLIAM A. GLASSON AND CHARLES S. TUESDAY

RECEIVED MAY 2, 1963

The kinetics of the thermal oxidation of nitric oxide in oxygen-nitrogen mixtures have been determined in the parts-per-million range by long-path infrared spectrophotometry. The results of this investigation indicate that the reaction is second order in nitric oxide, first order in oxygen, and independent of the concentration of added nitrogen dioxide, with a third-order rate constant, at 23°, of $(1.57 \pm 0.09) \times 10^{-9}$ p.p.m.⁻² min.⁻¹. In addition, it was found that there is no effect on the rate of the thermal oxidation due to either (a) addition of several olefins or (b) photolysis of the product nitrogen dioxide.

Introduction

The thermal oxidation of nitric oxide has been studied extensively²⁻⁵ over the past fifty years. These investigators established that reaction 1 is second order in nitric oxide and first order in oxygen and reported es-



entially the same value of the rate constant. The most recent⁶ investigation of the thermal oxidation, however, reports a greater than second-order dependence on nitric oxide concentration, an approximately first-order dependence on oxygen concentration, and a rate constant which is 50% of the previously reported value.²⁻⁵ In addition, a recent report⁷ of the rate of reaction 1 under atmospheric conditions yields a third-order rate constant which is approximately 200% of the literature value.²⁻⁵

In light of the reported inconsistencies concerning the order and rate constant of reaction 1 and because of the importance of reaction 1 in the atmospheric photooxidation of nitric oxide and hydrocarbons,⁸ a study of the thermal oxidation of nitric oxide, in the parts-per-million range, has been carried out.

In this investigation, the effects of nitric oxide, oxygen, and nitrogen dioxide concentrations on the rate of reaction 1 have been studied. In addition, the effects of added hydrocarbons and the photolysis of the product nitrogen dioxide have been investigated.

Experimental

Apparatus.—Analyses were made with a 3-m. base path multiple reflection cell used in conjunction with a modified Perkin-Elmer Model 21 infrared spectrophotometer. A path length of 120 m. was routinely used in this study. Irradiation was supplied by a number of black light fluorescent bulbs (F96TS/BL) mounted in the long-path cell. Details of the cell and the wave length distribution of the fluorescent lights have been given elsewhere.⁸

Procedure.—The long-path cell was evacuated to a pressure less than *ten microns*, a known amount of nitric oxide was then expanded into the cell from a glass vacuum system, and a known amount of additive (if any) was similarly added. A predetermined pressure of nitrogen was added to the cell and oxygen was then added to bring the final pressure to 760 mm. Timing was begun at the start of oxygen addition.

The rate of reaction 1 was followed by measuring the concentration of nitrogen dioxide as a function of time using one of two methods. For fast reaction rates, nitrogen dioxide was monitored continuously at 6.15 μ . Owing to the procedure employed and the pressure dependence of the nitrogen dioxide spectrum, accurate data could be obtained only after pressure equilibrium had been attained. It was estimated that, in the most rapid rates studied, not more than 5% of the reaction had occurred during this indeterminate period. For slow reaction rates, nitrogen dioxide was determined by repeated scanning of the region 4.5–8.5 μ followed by measurement of the absorption at 6.15 μ .

The absorptivities of nitrogen dioxide, methane, and *trans*-2-butene were determined by multiple calibrations based on manometric measurements. The absorptivity of 2,3-dimethyl-2-butene was determined by multiple calibrations made with a flame ionization detector. Concentrations reported are given in the units parts-per-million (p.p.m.) on a volume/volume basis.

Light intensity was measured by photolyzing very low concentrations of nitrogen dioxide in nitrogen and is expressed as the first-order rate constant for photolysis (K_d). The details and advantages of this method of light intensity measurement in the experimental system have been described previously.⁸

Results

The Effect of Initial Nitric Oxide and Oxygen Concentrations.—The effect of the initial nitric oxide concentration on the initial rate of reaction 1 under pseudo-second-order conditions has been determined at two oxygen concentrations, 2×10^5 and 2×10^4 p.p.m., over the range 2 to 50 p.p.m. nitric oxide. The results of this investigation are given in Table I and Fig. 1. The linearity of the plots in Fig. 1 indicates that the

(1) Presented in part at the 144th National Meeting of the American Chemical Society, Los Angeles, Calif., April 5, 1963.

(2) M. Bodenstein, *Z. Elektrochem.*, **24**, 183 (1918).

(3) G. Kornfeld and E. Klingler, *Z. physik. Chem.*, **B4**, 37 (1929).

(4) F. B. Brown and R. J. Crist, *J. Chem. Phys.*, **9**, 840 (1941).

(5) J. H. Smith, *J. Am. Chem. Soc.*, **65**, 74 (1943).

(6) J. C. Treacy and F. Daniels, *ibid.*, **77**, 2033 (1955).

(7) A. P. Altshuller, I. R. Cohen, S. F. Sleva, and S. L. Kopczynski, *Science*, **138**, 442 (1962). These authors reported a rate of $(5-7) \times 10^{-3}$ p.p.m. min.⁻¹ at a nitric oxide concentration of 3 p.p.m. in air at 1 atmosphere. Assuming the latter is an initial rate, the third-order rate constant is $(3-4) \times 10^{-9}$ p.p.m.⁻² min.⁻¹.

(8) C. S. Tuesday, "Chemical Reactions in the Lower and Upper Atmosphere," Interscience Publishers, Inc., New York, N. Y., 1961, pp. 15-49.

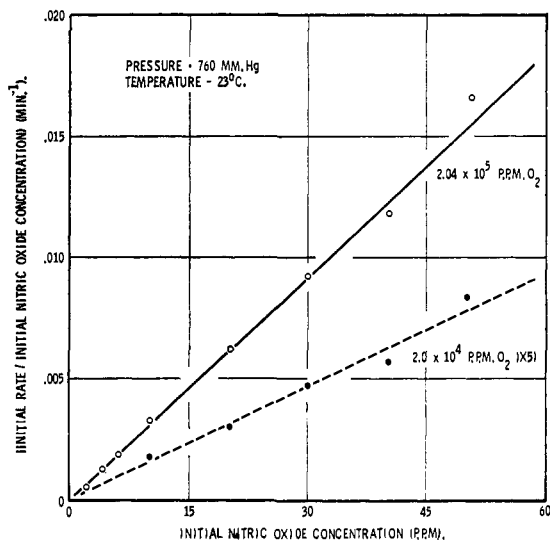


Fig. 1.—Effect of initial nitric oxide concentration on the initial thermal oxidation rate.

rate of reaction 1 is proportional to the second power of the initial nitric oxide concentration as has been observed previously²⁻⁵ under conditions of higher concentration and lower total pressure. Treacy and Daniels⁶ found an apparent order in nitric oxide of 2.3 at lower nitric oxide pressures which approached 2.0 at higher pressures.

TABLE I

THE RATE OF THE THERMAL OXIDATION OF NITRIC OXIDE AS A FUNCTION OF THE INITIAL CONCENTRATION OF NITRIC OXIDE^a

(O ₂), p.p.m.	(NO) ₀ , p.p.m.	R ₀ × 10 ² , ^b p.p.m. min. ⁻¹	k × 10 ⁹ , ^c p.p.m. ⁻² min. ⁻¹
2.04 × 10 ⁵	2.01	0.10	1.22
	4.06	0.51	1.59
	6.00	1.11	1.51
	10.0	3.27	1.60
	20.1	12.4	1.51
	29.9	27.5	1.51
	40.1	47.1	1.44
2.0 × 10 ⁴	50.6	84.1	1.61
	10.0	0.35	1.74
	10.1	0.34	1.70
	20.1	1.20	1.49
	29.9	2.83	1.42
	40.1	4.56	1.67
	50.2	8.42	1.58

^a At a total pressure of 760 mm. and a temperature of 23°.

^b The initial oxidation rate, R₀, was determined graphically from nitrogen dioxide *vs.* time plots. ^c The rate constant, k, was calculated from the third-order equation R₀ = k(O₂)(NO)₀².

The effect of oxygen concentration on the initial rate of reaction 1 has been determined with a large excess of oxygen relative to nitric oxide. The oxygen concentration was varied from 2 × 10⁴ to 6 × 10⁵ p.p.m. at a constant initial nitric oxide concentration of 10 p.p.m. The results of this study are given in Fig. 2. The linear plot of initial rate, R₀, *vs.* oxygen concentration indicates that the rate of reaction 1 is proportional to the first power of the oxygen concentration as has been observed previously²⁻⁶ under different experimental conditions. Treacy and Daniels⁶ found that the rate of reaction 1 was initially first order in oxygen but decreased to 0.8 order "after the reaction had proceeded to some small extent."⁹

The average value of the rate constant, k, for reaction 1 at 23° and one atmosphere pressure is

$$k = (1.57 \pm 0.09) \times 10^{-9} \text{ p.p.m.}^{-2} \text{ min.}^{-1}$$

(9) John C. Treacy, Ph.D. Thesis, University of Wisconsin, 1953, p. 60.

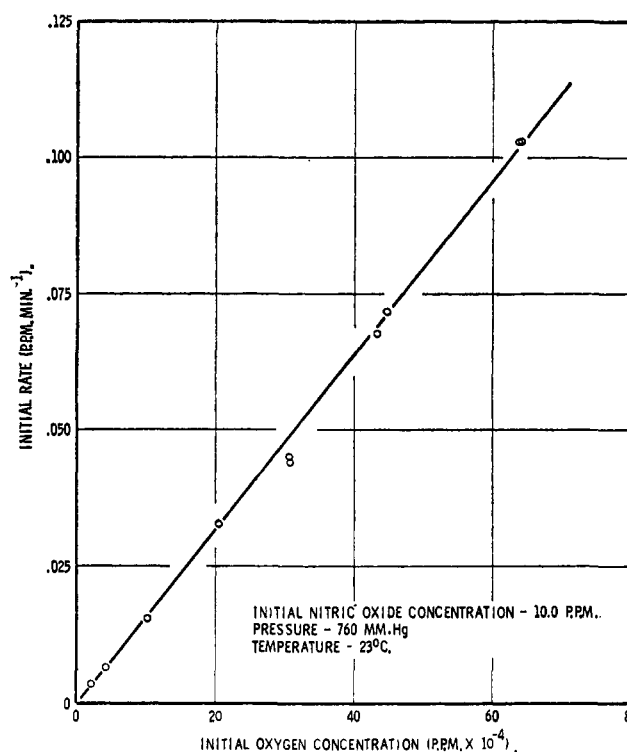


Fig. 2.—The effect of initial oxygen concentration on the initial thermal oxidation rate.

For comparative purposes, the value of k is given in c.g.s. units as: $k = (1.54 \pm 0.09) \times 10^4 \text{ l.}^2 \text{ mole}^{-2} \text{ sec.}^{-1}$. The data of Bodenstein² yield a value of k at 23° (interpolated¹⁰) of $1.49 \times 10^4 \text{ l.}^2 \text{ mole}^{-2} \text{ sec.}^{-1}$ at a total pressure of approximately 20 mm. Other investigators of reaction 1, in the pressure range 1–20 mm., reported values of k equal to $1.49 \times 10^4 \text{ l.}^2 \text{ mole}^{-2} \text{ sec.}^{-1}$ (25°),⁴ $1.2 \times 10^4 \text{ l.}^2 \text{ mole}^{-2} \text{ sec.}^{-1}$ (25°),⁵ and $1.4 \times 10^4 \text{ l.}^2 \text{ mole}^{-2} \text{ sec.}^{-1}$ (21°).³ The agreement of the value determined in this study with the cited literature values is generally within the experimental error of the various determinations with one exception. The results of a recent study⁶ indicate a value of k equal to $7.5 \times 10^3 \text{ l.}^2 \text{ mole}^{-2} \text{ sec.}^{-1}$. The latter authors have indicated that reaction 1 exhibits a rate increase after 25% reaction and attribute the disagreement of their rate constant value with those in the literature to the fact that previous studies involved determination of k over a large fraction of the reaction. In an attempt to verify the apparent rate increase reported by Treacy and Daniels, several oxidations of nitric oxide were followed to approximately 25–35% reaction. The results of the latter experiments, as shown in Fig. 3, indicated no deviation from the pseudo-second-order kinetics expected on the basis of the simple third-order reaction with a large excess of oxygen. The latter observations cast considerable doubt on the applicability of Treacy and Daniels' conclusions to the atmospheric situation.

The Effect of Initial Nitrogen Dioxide Concentration.

—The effect of the concentration of added nitrogen dioxide on the initial rate of reaction 1 has been investigated. The results are given in Table II.

The data indicate that there is no influence of added nitrogen dioxide on the initial rate of reaction 1. Previous investigators^{2,3} have reached the same conclusion,

(10) When the data of ref. 2, from 0 to 90°, were plotted as log k *vs.* 1/T, arithmetic errors were found in the values of k. The data were recalculated and the values obtained agreed with the recent tabulation of Leighton of the same data: P. A. Leighton, "Photochemistry of Air Pollution," Academic Press, Inc., New York, N. Y., 1961, p. 185.

TABLE II

THE EFFECT OF ADDED NITROGEN DIOXIDE ON THE INITIAL RATE OF THE THERMAL OXIDATION OF NITRIC OXIDE^a

(NO) ₀ , p.p.m.	(NO ₂) ₀ , p.p.m.	R ₀ × 10 ³ , ^b p.p.m. min. ⁻¹	k × 10 ⁷ , ^c p.p.m. ⁻² min. ⁻¹
4.06	..	5.10	1.59
4.00	1.00	4.97	1.52
3.94	2.00	5.25	1.66
4.00	2.99	4.94	1.51

^a The runs were performed at a total pressure of 760 mm., a temperature of 23°, and an oxygen concentration of 2.04 × 10⁵ p.p.m. ^b The initial oxidation rate, R₀, was determined graphically from plots of nitrogen dioxide vs. time. ^c The rate constant, k, was calculated from the third-order equation R₀ = k(O₂)(NO)₀².

with the exception of Treacy and Daniels⁶, who reported a slight inhibitory effect of added nitrogen dioxide.

The Effect of Added Olefin.—The effect of added olefins on the initial rate of reaction 1 has been investigated at initial concentrations of nitric oxide from 2 to 10 p.p.m. The olefins studied, 2,3-dimethyl-2-butene and *trans*-2-butene, were at concentrations of 5–10 p.p.m. The results of this study are given in Table III. Under the conditions employed in this investigation there is no effect of these added olefins on the initial rate of reaction 1. To the authors' knowledge, there are no data in the literature pertaining to comparable systems.

TABLE III

THE EFFECTS OF ADDED OLEFIN AND NITROGEN DIOXIDE PHOTOLYSIS ON THE INITIAL RATE OF THE THERMAL OXIDATION OF NITRIC OXIDE^a

(Hydrocarbon) ₀ , p.p.m.	(NO) ₀ , p.p.m.	R ₀ × 10 ³ , ^b p.p.m. min. ⁻¹	k × 10 ⁹ , ^c p.p.m. ⁻² min. ⁻¹
2,3-Dimethyl-2-butene			
5.06	9.94	33.2	1.63
5.05	6.00	11.1	1.51
10.4	5.99	11.2	1.53
5.06	1.99	1.08	1.34
<i>trans</i> -2-Butene			
10.0	5.97	10.6	1.46
10.0	3.98	5.19	1.61
Nitrogen dioxide photolysis ^d			
...	3.94	5.03	1.59
...	1.99	1.13	1.40
50.2 (methane) ^e	2.02	1.37	1.65

^a The runs were performed at a total pressure of 760 mm., a temperature of 23°, and an oxygen concentration of 2 × 10⁵ p.p.m. ^b The initial rate, R₀, was determined graphically from plots of nitrogen dioxide vs. time. ^c The rate constant, k, was calculated from the third-order equation R₀ = k(O₂)(NO)₀². ^d The light intensity, K_d(NO₂), was equal to 0.29 min.⁻¹. ^e In addition to the 3 p.p.m. methane impurity present in the experimental mixture.

The Effect of Nitrogen Dioxide Photolysis.—A limited number of experiments were performed in order to establish whether the photolysis of nitrogen dioxide, formed in reaction 1, had an effect on the thermal oxidation rate. The results of this study are given in Table III. There is no effect due to the irradiation on the thermal rate within the experimental error of the measurements. The oxygen which was used in this study has an average methane concentration of 15 p.p.m., which corresponds to 3 p.p.m. of methane in the experimental mixtures. The photoxidation of nitric oxide is promoted by many hydrocarbons¹¹ and therefore any promotional effect of the methane impurity may offset a possible inhibitory effect of the nitrogen dioxide photolysis. In order to test this possibility, the rate of nitrogen dioxide formation was determined

(11) Reference 9, p. 258.

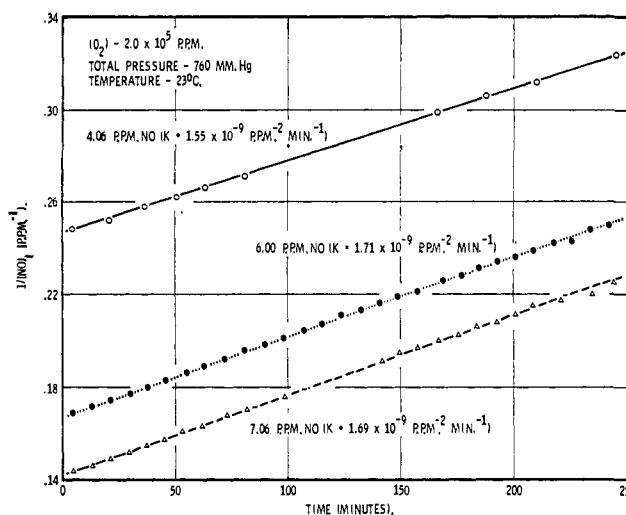
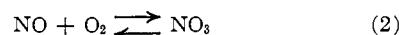


Fig. 3.—Test of pseudo-second-order rate law: $1/(\text{NO})_t = 1/(\text{NO})_0 + K(\text{O}_2)t$.

in an irradiated system containing 2 p.p.m. of nitric oxide, 2 × 10⁵ p.p.m. of oxygen, and 50 p.p.m. of added methane. As indicated in Table III, the added methane had no effect on the rate of nitrogen dioxide formation within the experimental error of our measurements.

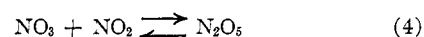
Discussion

The results of this investigation are consistent with the mechanism suggested by Trautz¹²



which is kinetically equivalent to the reaction scheme suggested by Bodenstein² wherein the dimer of nitric oxide, (NO)₂, reacts with oxygen to yield nitrogen dioxide. The mechanism of Trautz is preferred since evidence has been reported¹³ for the existence of NO₃. The complex mechanism recently hypothesized by Treacy and Daniels,⁶ involving the intermediate formation of the species (NO₃·NO), is not necessary to explain the results of this investigation.

The lack of dependence of the initial rate of oxidation on the initial concentration of nitrogen dioxide indicates that reaction 4 is not important under our experi-

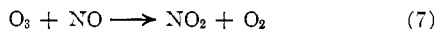
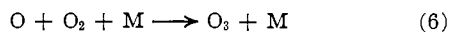
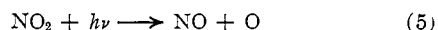


mental conditions. This conclusion is consistent with the results of a recent study of the nitric oxide–nitrogen pentoxide system¹⁴ which indicated that the value¹⁵ of k_4/k_3 was 0.069 at 23°. Thus, under the most favorable conditions for inhibition used in the present investigation (nitrogen dioxide/nitric oxide = 3/4) the ratio of the rates of reactions 4 to 3 would be 0.052, which is negligible.

The absence of any effect of added olefin on the initial oxidation rate suggests that the olefin does not interfere with reactions 2 and 3. This result also suggests that under our experimental conditions the reaction of olefin with nitrogen dioxide is not important, which is in agreement with the results of Ford and Endow.¹⁶

(12) M. Trautz, *Z. Elektrochem.*, **22**, 104 (1916).(13) E. J. Jones and O. R. Wulf, *J. Chem. Phys.*, **5**, 873 (1937).(14) I. C. Hisatsune, B. Crawford, Jr., and R. A. Ogg, Jr., *J. Am. Chem. Soc.*, **79**, 4648 (1957).(15) A more recent determination of this ratio indicates a value of 0.3: G. Schott and N. Davidson, *ibid.*, **80**, 1841 (1958). This value was determined at high temperatures by the shock-tube method and therefore a rather large extrapolation is necessary to obtain a value at 23°.

The lack of an effect on the initial rate of thermal oxidation due to the photolysis of nitrogen dioxide can be explained in terms of reactions 5-7.



The rapid rate of reaction 6¹⁷ is sufficient to convert all the oxygen atoms formed in reaction 5 to ozone. However, the rate of reaction 7 is sufficiently fast¹⁸ to remove

(16) H. W. Ford and N. Endow, *J. Chem. Phys.*, **27**, 1277 (1957).

(17) $k_6(\text{O}_2)(\text{M})$ is equal to $2.4 \times 10^4 \text{ sec.}^{-1}$ at 25°, in air at one atmosphere pressure: S. W. Benson and A. E. Axworthy, Jr., *ibid.*, **26**, 1718 (1957).

(18) k_7 is equal to $1.17 \times 10^{17} \text{ l. mole}^{-1} \text{ sec.}^{-1}$ at 25°: H. S. Johnston and H. J. Crosby, *ibid.*, **22**, 689 (1954).

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY, PRINCETON, N. J.]

Microwave Absorption and Molecular Structure in Liquids. LII. Charge-Transfer Complexes^{1,2}

By JAMES E. ANDERSON³ AND CHARLES P. SMYTH

RECEIVED MAY 27, 1963

Measurements of the dielectric constant and loss of five charge-transfer systems have been carried out at various wave lengths between 1.25 and 40 cm. Dilute solutions of iodine in benzene and *p*-dioxane gave extremely small relaxation times, which are attributed to a rapid exchange mechanism. The kinetics of this mechanism are discussed and related to relaxation behavior. Triethylamine, tributylamine, and triphenylamine complexes with 1,3,5-trinitrobenzene were measured in dilute *p*-dioxane solution at 35°. Relaxation studies indicate that the triethylamine and tributylamine complexes are stable and dipolar. No evidence of a dipolar molecular complex between triphenylamine and 1,3,5-trinitrobenzene was observed. The possibility of different types of complexes is discussed.

Introduction

The recent literature contains a number of studies of charge-transfer complexes. On the basis of low frequency (static) dielectric measurements, the "apparent dipole moments" of many of these complexes have been determined.⁴ The common usage of the term dipole moment implies some sort of polar species which orients in the applied field. In certain charge-transfer systems, the existence of such a polar species has not yet been unambiguously demonstrated.

Atomic, electronic, and orientational terms may contribute to the observed static polarization of a liquid. Only molecules having permanent dipole moments possess an orientation polarization, while both polar and nonpolar molecules have atomic and electronic polarization. A dispersion associated with the atomic and electronic terms is manifest in the familiar infrared, visible, and ultraviolet absorption. For simple polar molecules in the liquid state, the dispersion region connected with orientation polarization occurs at microwave frequencies. For this reason, the presence or absence of a true polar species in a liquid system may be established through dielectric measurements in this frequency range.

Experimental

Purification of Materials.—U.S.P. resublimed iodine, obtained from the Baker and Adamson Co., was used without further purification. Reagent benzene and *p*-dioxane were purified by refluxing overnight above sodium and then distilled. The refractive indices, n_D^{20} , were 1.50084 and 1.42259, respectively. Triethylamine, obtained from Matheson, Coleman and Bell, was

purified by distillation; n_D^{20} 1.39958. Tributylamine was obtained from the Eastman Kodak Co. and was distilled under vacuum; n_D^{20} 1.42898. Triphenylamine was obtained from the Eastman Kodak Co. and was used without further purification; m.p. 125.0-125.6°.

Treatment of Data and Experimental Results.—The experimental data for the iodine-benzene and iodine-*p*-dioxane complexes were treated by a modification of the method previously described.⁵ The equilibrium constant for each system⁶ was used to calculate the mole fraction of complex in each of six solutions. The slopes a' and a'' for each frequency were then calculated on the basis of change in dielectric constant and dielectric loss with mole fraction of complex. Since the dielectric loss is concerned only with the polar species present, this correction was necessary to account for the appreciable amount of noncomplexed, nonpolar iodine present in the system. The data are shown in Table I. The two-component systems of triethylamine, tributylamine, triphenylamine, and 1,3,5-trinitrobenzene in dilute *p*-dioxane solution were treated in the usual manner.⁵ Five solutions and the solvent were measured in each determination. Triethylamine, tributylamine, and triphenylamine were each mixed with 1,3,5-trinitrobenzene in dilute dioxane solution. Each tertiary solution was made up keeping the particular amine and trinitrobenzene in a 1:1 mole ratio. The a' and a'' slopes were then determined by plotting the dielectric constant and loss vs. mole fraction of a 1:1 complex. The data and results are presented in Tables II and III.

Acknowledgment.—The authors wish to acknowledge the valuable assistance of Jerome Zemla in obtaining the data and preparing the manuscript.

Apparatus.—The apparatus and measuring techniques have been described in previous papers.⁷⁻¹⁰

Discussion of Experimental Results

Complexes of Iodine.—Apparent dipole moments for iodine in nonpolar organic solvents have been reported by many observers.⁴ Fairbrother¹¹ has determined apparent moments of 1.3 and 0.6 D. for iodine in *p*-dioxane and benzene, respectively. Owing to the geom-

(5) A. D. Franklin, W. M. Heston, Jr., E. J. Hennelly, and C. P. Smyth, *J. Am. Chem. Soc.*, **72**, 3447 (1950).

(6) G. Briegleb, ref. 4, pp. 124-125.

(7) W. M. Heston, Jr., E. J. Hennelly, and C. P. Smyth, *J. Am. Chem. Soc.*, **70**, 4093 (1948).

(8) H. L. Laquer and C. P. Smyth, *ibid.*, **70**, 4097 (1948).

(9) W. M. Heston, Jr., A. D. Franklin, E. J. Hennelly, and C. P. Smyth, *ibid.*, **72**, 3443 (1950).

(10) D. A. Pitt and C. P. Smyth, *J. Phys. Chem.*, **63**, 582 (1959).

(11) F. Fairbrother, *J. Chem. Soc.*, 1051 (1948).

(1) This research was supported by the National Science Foundation.

(2) This paper represents part of the work submitted by J. E. Anderson to the Graduate School of Princeton University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(3) American Machine and Foundry Fellow, 1961-1962; National Science Foundation Cooperative Fellow, 1962-1963; National Science Foundation Summer Fellow, 1963.

(4) G. Briegleb, "Elektronen-Donator-Acceptor-Komplexe," Springer-Verlag, Berlin, 1961, pp. 13-20.