Solvent Effects on the Electronic Absorption Spectrum of Nitrite Ion[1]

BY S. J. STRICKLER[2] AND M. KASHA

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The electronic absorption spectrum of nitrite ion has been measured from 1900 to 4300 Å. at room temperature in four solvents of differing polarity. The measured band shifts and intensities provide evidence for the assignment of the electronic transitions. The two weak bands near 3600 and 2800 A., respectively, are assigned as $n \rightarrow \pi^*$ transitions, and the intense band near 2100 Å. as a $\pi \rightarrow \pi^*$ transition. Our conclusions are in agreement with previous results on crystal spectra and with theoretical calculations.

The near-ultraviolet spectrum of nitrite ion, NO_2^-, has been known for some time, but the interpretation of the three observed bands has not been clear. Rather qualitative theoretical considerations by Mulliken[3] and by Walsh[4] have shown that likely low-lying transitions would involve promotion of electrons from a π-orbital or from various nonbonding orbitals to an antibonding π-orbital. Experimental studies of crystal spectra have been made by Sidman[5] and Trawick and Eberhardt.[6] They have assigned the weak bands to $n \rightarrow \pi^*$ transitions and the intense band to a $\pi \rightarrow \pi^*$ transition. On the other hand, Friedman[7] and Stein and Treinen[8] have considered the strong band to be due to an "electron transfer" type of transition rather than to any intrinsic transition of the ion. The specific nature of the $n \rightarrow \pi^*$ transitions in nitrite ion has also been a subject of disagreement.[9,10]

Because of this situation, we have measured the effects of different solvents on the ultraviolet spectrum of nitrite ion. Such studies have often been useful in assigning transitions in organic molecules, and similar techniques are applicable to many inorganic molecular ions. This type of study is complementary to the previous work on crystal spectra, and we believe that it provides good evidence of the nature of the orbitals involved in the transitions.

Experimental

For reasons of solubility, we have used tetramethylammonium nitrite for this study. This was prepared from pure grades of sodium nitrite and tetramethylammonium iodide by the use of a column of anion-exchange resin. The spectrum of the tetramethylammonium nitrite in water appears to be identical with that of sodium nitrite.

The solvents used were N,N-dimethylformamide (DMF), acetonitrile, absolute ethanol, and water; DMF was purified by distillation over Drierite through a column packed with glass helices. A fraction boiling at a constant temperature of 152° was collected for use as the solvent. Eastman Spectro Grade acetonitrile was used from a freshly opened bottle without further purification. Commercial absolute alcohol was freed from traces of benzene and toluene by slow fractional distillation and was used freshly distilled. Water was redistilled from alkaline permanganate solution.

All spectra were measured using a Cary Model 14 spectrophotometer. They were run at room temperature, using matched quartz absorption cells with path lengths varying from 5 cm. to 0.1 mm. For spectra in the region of wave lengths shorter than 2000 Å., the light path of the spectrophotometer was flushed with nitrogen.

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(5) J. W. Sidman, J. Am. Chem. Soc., 79, 2669 (1957).

(6) W. G. Trawick and W. H. Eberhardt, J. Chem. Phys., 22, 1462 (1954).

(7) H. L. Friedman, ibid., 21, 319 (1953).

(8) G. Stein and A. Treinen, Trans. Faraday Soc., 55, 1086 (1959).

(9) S. P. McGlynn and M. Kasha, J. Chem. Phys., 24, 481 (1956).

(10) J. W. Sidman, Chem. Rev., 58, 689 (1958).

Results and Discussion

The spectra obtained are shown in Fig. 1. The weak and strong bands are drawn to different scales to show the details of each. Three distinct regions of absorption are apparent: two weak bands near 3600 and 2800 Å., and a strong band near 2100 Å. For convenience, we have labeled these bands as I, II, and III, respectively. The frequencies and intensities of the bands are summarized in Table I.

TABLE I

SUMMARY OF THE SPECTRA OF TETRAMETHYLAMMONIUM NITRITE IN FOUR SOLVENTS

Solvent	Band I $\bar{\nu}_{max}$, cm.$^{-1}$	ϵ_{max}	Band II $\bar{\nu}_{max}$, cm.$^{-1}$	ϵ_{max}	Band III $\bar{\nu}_{max}$, cm.$^{-1}$	ϵ_{max}
DMF	26,890	27.6	Missing	...	....	..
CH$_3$CN	27,000	24.2	Missing	...	46,730	6180
EtOH	28,060	29.5	Ca. 35,200	9.3	47,080	5160
H$_2$O	28,200	22.5	Ca. 34,800	9.4	47,620	5380

Simple LCAO–MO treatments of nitrite ion (and similar molecules) have been presented by Mulliken,[3] Walsh,[4] and Sidman,[5] which are useful in interpreting the spectra. Schematic pictures of the orbitals are also given by Sidman, who suggested that the most likely transitions to appear at low energies were: $n_N \rightarrow \pi^*(B_1)$, $n_O \rightarrow \pi^*(A_2)$, $\pi \rightarrow \pi^*(B_2)$, and $n_O \rightarrow \pi^*(B_1)$. Here the symmetries of the excited states have been given in parentheses. We use the accepted designation,[11] where the molecule is taken to lie in the yz-plane with z the principal axis. Sidman[5] used a different convention, with the result that B_1 and B_2 symmetries are interchanged in his paper. The symbols n_N and n_O refer to nonbonding orbitals on the nitrogen and oxygen atoms, respectively.

We shall now discuss the assignment of the individual bands.

Band I.—Sidman's study of absorption and fluorescence of crystalline sodium nitrite[5] showed that the lowest energy band was allowed by intrinsic molecular symmetry. On this basis he assigned this band as the $n_N \rightarrow \pi^*$ transition. Trawick and Eberhardt[6] came to the same conclusion on the basis of the polarization, and the fact that the band is not observed in nitrate ion and in nitromethane.

One argument against this interpretation is the low intensity of the band. The n_N-orbital visualized by Sidman would have considerable 2s-character, and the $n_N \rightarrow \pi^*$ transition would fall into the class designated as $^1W \leftarrow ^1A$ by Platt.[12] Such a band is allowed by the local symmetry conditions at the nitrogen atom and should be considerably more intense than is observed for band I. Sidman realized this problem, and in a later paper[10] suggested that it might be an $n_O \rightarrow \pi^*$ transition.

In our spectra in different solvents, it is seen that band I shifts to the blue in the hydrogen-bonding sol-

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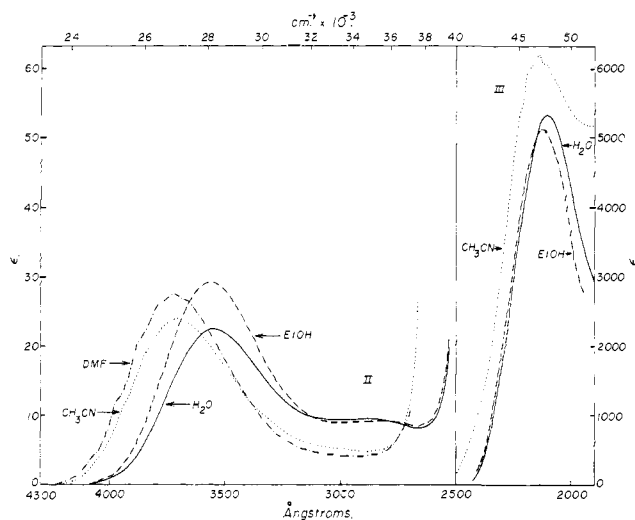
(12) J. R. Platt, J. Opt. Soc. Am., 43, 252 (1953).

Fig. 1.—Spectra of tetramethylammonium nitrite in N,N-dimethylformamide (DMF), acetonitrile, water, and ethanol at room temperature.

vents when compared with the spectra in the more inert solvents DMF and acetonitrile. Such a blue shift is characteristic of n → π^* transitions when hydrogen bonds are formed to the atom on which the nonbonding orbital is located. It occurs because the presence of the positive hydrogen atom makes it more difficult to remove the electron from the nonbonding orbital and place it in the more delocalized π-orbital.

In nitrite ion we expect strong hydrogen bonds to be formed at the oxygen atoms which are highly negative, but little or no hydrogen bonding at the nitrogen atom. Thus the blue shift of band I is not consistent with an interpretation as an n_N → π^* transition, but would indicate an n_O → π^* transition.

The answer to the question of interpretation of this band seems to have been given by the recent work of McEwen,[13] who has made careful quantitative calculations of the orbitals and states of nitrite ion. She finds that the highest filled orbital of a_1 symmetry is not primarily a nitrogen nonbonding orbital, but is actually about 80% localized on the oxygen atoms. This being true, the promotion of an electron from this orbital to the π^*-orbital would be an x-polarized, allowed transition, but it would be expected to be weak (^1U ← ^1A in Platt's notation[12]) and to shift to the blue in hydrogen-bonding solvents. This agrees well with all the experimental observations, so band I can be quite definitely assigned to an n → π^* transition of symmetry $^1B_1$ ← $^1A_1$.

Band III.—It is convenient to discuss next the intense band near 2100 Å. This has usually been assumed to be the π → π^* transition, as that is the only molecular transition expected to lie at these low energies and to have a high intensity. Trawick and Eberhardt[6] studied the band in crystalline sodium nitrite and found it to be y-polarized, which would correspond to the symmetry of the π → π^* transition. However, others have suggested that this band is due to an "electron transfer" type of transition.[7,8]

Transitions of the latter type occur in the spectra of halide ions in solution. The detailed nature of the transition in these cases is unclear, but the solvent molecules appear to be intimately involved. The solvent effects are very large and seem to be characteristic of this type of transition.[14] Shifts of about 5000 cm.$^{-1}$ are found when the solvent is changed from aceto-

nitrile to hydroxylic solvents, and the energies of the transitions increase in the order CH_3CN < H_2O < EtOH. This is quite different from the solvent effects found for the strong band of nitrite ion, and we believe this to be proof that the latter is not an "electron transfer" band.

Band III does show a significant blue shift in the hydrogen-bonding solvents, similar to that found for the n → π^* transition. But in nitrite ion, the highest filled π-orbital actually has the nature of a nonbonding orbital, since it is completely localized on the oxygen atoms. The π → π^* transition would have to remove partly an electron from the oxygen atoms in the same way as an n_O → π^* transition, so a blue shift of the band would be expected in hydrogen-bonding solvents. Thus we confirm the conclusion of Trawick and Eberhardt, and assign band III to the π → π^* transition of symmetry $^1B_2$ ← $^1A_1$.

Another strong band seems to have developed as a shoulder on the high energy side of band III in acetonitrile solution, lying somewhere below 1900 Å. This does not appear in the spectra in water or ethanol, presumably lying at much higher energies. We suggest that this fourth band may actually be the "electron transfer" band of nitrite ion, as this would be expected to lie in this region, to be quite intense, and to occur at much higher energies in water and ethanol than it would in acetonitrile.

Band II.—Band II of the spectrum of nitrite ion behaves in a rather peculiar fashion. It is observed as a weak shoulder between bands I and III in ethanol and water, appearing to lie at slightly lower energy in the latter. However, in DMF and acetonitrile, band II appears entirely unresolved. It must have either decreased in intensity or have moved to much higher energies so as to be hidden beneath band III.

It seems most likely that this band should be ascribed to the n_O → π^* transition of symmetry $^1A_2$ ← $^1A_1$, which is forbidden. Such a band should not lie at lower energies in hydroxylic solvents than in more inert solvents, so if this assignment is correct, it must be much weaker in the inert solvents. The explanation for this may be found in the following argument.

This n_O → π^* transition in nitrite ion is forbidden by molecular symmetry, as it is $^1A_2$ ← $^1A_1$. Such forbidden transitions in molecules usually still appear with small intensity because asymmetric molecular vibrations perturb the electronic distribution and permit the forbidden transition to borrow intensity from other allowed transitions. The formal method of treating this by perturbation theory has been given by Herzberg and Teller.[15] However, in a triatomic, C_{2v} molecule like nitrite ion, the only asymmetric vibration has symmetry b_2. Under a b_2 perturbation, the $^1A_2$ ← $^1A_1$ transition cannot borrow intensity from the nearby, intense π → π^* transition, which has $^1B_2$ ← $^1A_1$ symmetry. This means that, under vibrational perturbation, it can only borrow intensity from the weak band I or from other transitions lying much higher in energy. This may account for the very low intensity as observed in DMF and acetonitrile.

When the nitrite ion is dissolved in ethanol or water, however, the hydrogen bonds formed may also perturb the electronic distribution. Since there is no symmetry limitation on the hydrogen bonds formed, this type of perturbation could mix the $^1A_2$ excited state with a $^1B_2$ excited state, with the result that the transition would borrow intensity from the π → π^* transition, and would appear with greater intensity. This situation would then be analogous to the lowest band of nitrate

(13) K. L. McEwen, J. Chem. Phys., 34, 547 (1961).
(14) S. J. Strickler and M. Kasha, ibid., 34, 1077 (1961).

(15) G. Herzberg and E. Teller, Z. physik. Chem. (Leipzig), B21, 410 (1933).

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.

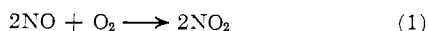# The Atmospheric Thermal Oxidation of Nitric Oxide[1]

BY WILLIAM A. GLASSON AND CHARLES S. TUESDAY

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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 extensively[2-5] over the past fifty years. These investigators established that reaction 1 is second order in nitric oxide and first order in oxygen and reported essentially the same value of the rate constant. The most recent[6] 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 report[7] 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]

$$2NO + O_2 \longrightarrow 2NO_2 \qquad (1)$$

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 photo-oxidation 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.

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

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(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.

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 (F96T8/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