

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

Absorption Spectra of Nitric Oxide in Solutions

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RECEIVED AUGUST 7, 1962

The absorption spectra of nitric oxide in aromatic and aliphatic hydrocarbons, in alcohols and in water were investigated. The experimental results show that the broad structureless absorption bands observed rise from charge transfer between the solvent and NO. Thermochemical data indicate that the solvent-NO interactions are due to contacts in solution without the formation of a stable complex. The charge transfer spectra of NO and O₂ solution are compared. The enhancement of singlet-triplet transitions of benzene and the quenching mechanism of triplet states by NO are considered briefly.

Introduction

Recently the absorption spectra of oxygen in solution were investigated in detail.¹⁻⁴ Aromatic solvents reveal enhanced singlet-triplet transitions due to configuration interaction with the excited singlet^{2,5} and the charge transfer state.^{2,6} In all cases strong featureless bands are observed, which on the basis of spectroscopic² and thermochemical^{2,3} data can be assigned to contact charge transfer spectra.⁷ Other paramagnetic molecules, characterized by positive electron affinity, are expected to produce effects similar to oxygen. Nitric oxide is an obvious example, and in fact a continuous absorption band of NO in methanol was observed and assigned to a charge transfer spectrum.³ Recently absorption bands of NO in polar solvents (*e.g.*, methanol and acetonitrile) in the region 380-320 m μ were reported,⁸ being assigned to spin-forbidden transitions of NO in solution.⁸ In the present work the absorption spectra of NO in aliphatic and aromatic hydrocarbons, in alcohols and in water were investigated.

Experimental

Materials and Gases.—Benzene, toluene, anisole, acetone, methanol and ethanol of analar grade and acetonitrile, diethyl ether and cyclohexane of Eastman "spectro" grade were used. Methanol and ethanol were purified by refluxing with diphenylhydrazine and magnesium metal and finally distilled from calcium oxide. Dimethylaniline was purified by distillation from 5% acetic anhydride and was stored over ethylenediaminetetraacetate. The water was triply distilled from alkaline permanganate and from phosphoric acid.

Nitric oxide (Matheson product) was purified from traces of NO₂ and N₂O₃ by bubbling through sodium hydroxide solution, and dried over calcium chloride. Finally the gas was purified by trap to trap distillation *in vacuo*. This purification method leads to satisfactory reproducible results.

Spectrophotometric Measurements.—One half cm. and 4 cm. quartz absorption cells were used. The absorption cells were equipped with an attachment for evacuation on a vacuum line. Measurements were carried out using a Hilger Uvispek spectrophotometer and an Optica CF 4 recording spectrophotometer. Optical densities were measured against air as reference. All measurements were carried out at room temperature (22°).

Preparation of Solutions and Procedure.—The solvents in the absorption cells were evacuated on a vacuum line through a liquid air trap until the pressure of the uncondensable gases did not exceed 10⁻³ mm. The pumping system then was disconnected and the solution was connected to the vacuum line and saturated with NO for 2 hr. The partial pressure of NO above the solution was in the region $P_{NO} = 100-500$ mm. During the evacuation and the saturation processes the solution was stirred with a glass coated magnetic stirrer. The absorption spectra of the solutions were taken in the order: (a) evacuated, (b) NO saturated, (c) evacuated again.

Estimation of Solubility Data for NO.—For the calculation of the apparent molar absorption coefficients of NO in solution, its concentration has to be determined. From the available solubility data for NO and O₂ in water methanol, ethanol and ben-

zene⁹ the ratio of the Bunsen solubility coefficients B for these two gases in these solvents is $B(NO)/B(O_2) = 1.8 \pm 0.1$ at 20°. Using this factor and the solubility data for O₂ in diethyl ether⁹ and dimethylaniline¹⁴ $B(NO)$ for these solvents was estimated. The solubility of NO in toluene and anisole was taken to be equal to that in benzene.⁹ $B(NO)$ in cyclohexane was estimated from $B(O_2)$ in cyclohexanol and in petroleum ether. The solubility in acetonitrile was roughly estimated from $B(O_2)$ in ethyl acetate.⁹ These estimates are summarized in Table I.

TABLE I
BAND ONSET ENERGIES FOR NO SOLUTIONS

Solvent	$B(NO)$	λ ($\epsilon = 10$), m μ	$h\nu$ ($\epsilon = 10$), eV.
1 Dimethylaniline	0.2	241.6	2.95
2 Anisole	.25	330	3.75
3 Toluene	.25	287.5	4.32
4 Benzene	.27	283	4.36
5 Diethyl ether	.7	241.6	5.13
6 Cyclohexane	.6	228	5.4
7 Methanol	.35	232.6	5.32
8 Ethanol	.26	235.4	5.26
9 Acetonitrile	.3	234	5.28
10 Water	.043	238	5.18

Results

The optical absorption of gaseous NO at 600 mm. in a 1 cm. cell was found to be negligible in the region 500-230 m μ , in agreement with previous data.^{10,11} The absorption spectra of NO in some solvents are presented in Fig. 1. The absorption caused by NO disappears on evacuating the solutions. Thus, we conclude that these absorption bands are due to some interaction of NO and the solvent and not to chemical products. These absorption bands due to NO are diffuse, showing a marked dependence on the nature of the solvent. In the case of benzene an additional weak absorption showing a vibrational fine-structure was observed (Fig. 2), in agreement with the results of Evans.¹ Of all the solvents investigated in the present work, acetone was exceptional as no absorption of NO in this solvent could be detected.

The contribution of the dissolved nitric oxide to the optical absorption is obtained by subtracting the optical density D_0 of the evacuated solvent from the optical density D of the NO solution. The apparent molar absorption coefficient of NO in solution is obtained from

$$\epsilon = (D - D_0)/Cl \quad (1)$$

where l is the cell length and C is the NO concentration estimated from the solubility data.

In some cases, *e.g.*, NO solutions in H₂O, methanol and dimethylaniline, the dependence of $D - D_0$ on nitric oxide concentration was investigated. ϵ was found to be independent of NO concentration (within $\pm 20\%$) in the region $P_{NO} = 100-500$ mm.

(9) A. Seidel, "Solubility of Inorganic Compounds," D. Van Nostrand Co. New York, N. Y., 1940.

(10) F. F. Maro, *J. Opt. Soc. Am.*, **43**, 1186 (1953).

(11) G. W. Bethke, *J. Chem. Phys.*, **31**, 662 (1959).

(1) D. F. Evans, (a) *J. Chem. Soc.*, 345 (1953); (b) 1351 (1957); (c) 3855 (1957); (d) 1987 (1961).

(2) H. Tsubomura and R. S. Mulliken, *J. Am. Chem. Soc.*, **82**, 5966 (1960).

(3) J. Jortner and U. Sokolov, *J. Phys. Chem.*, **65**, 1633 (1961).

(4) E. C. Lim and V. L. Kowalski, *J. Chem. Phys.*, **46**, 1729 (1962).

(5) J. Hoijtink, *Mol. Phys.*, **3**, 67 (1960).

(6) J. N. Murrel, *ibid.*, **3**, 319 (1960).

(7) L. E. Orgel and R. S. Mulliken, *J. Am. Chem. Soc.*, **79**, 4389 (1957).

(8) T. S. Piper and R. S. Drago, *J. Chem. Phys.*, **36**, 241 (1962).

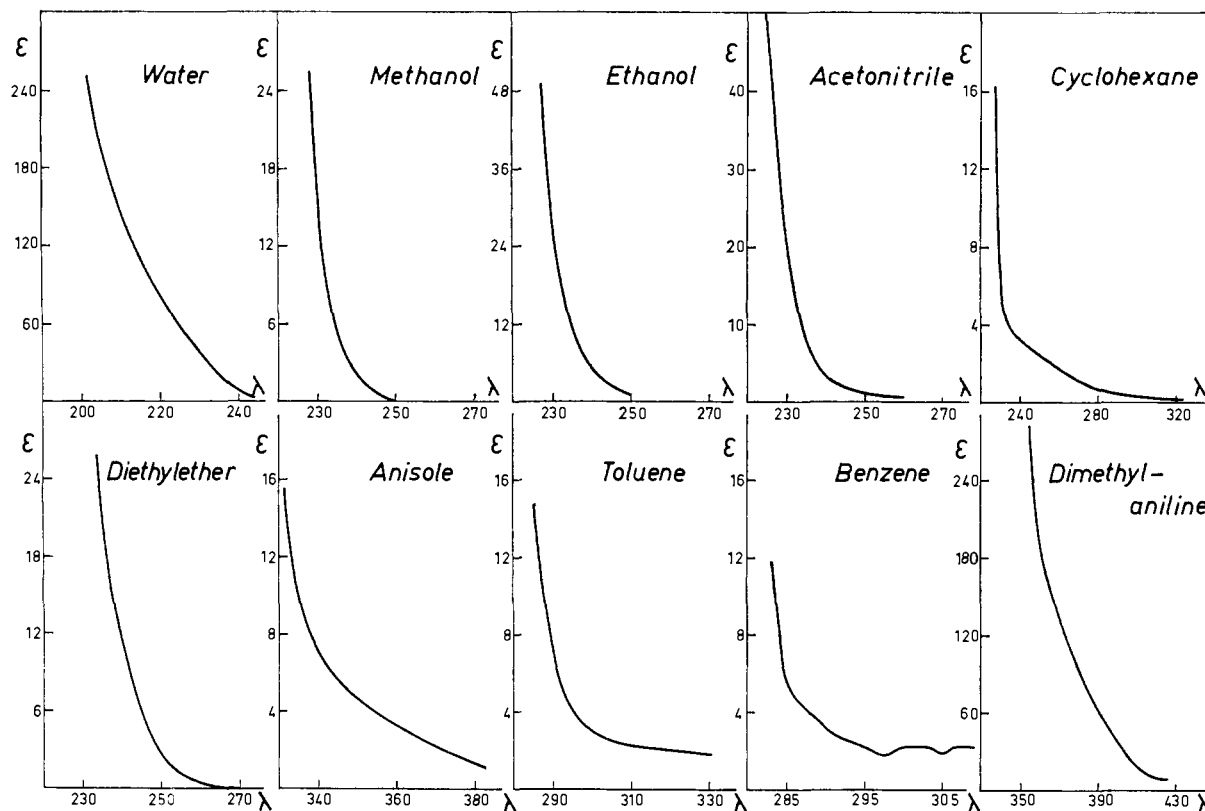


Fig. 1.—Absorption spectra of NO in solutions at 22°: ϵ in liter mole⁻¹ cm.⁻¹ and λ in m μ .

The spectra presented in Fig. 1 were measured to the shortest measurable wave lengths in 4 cm. cells; H₂O, cyclohexane and dimethylaniline were also measured in 0.5 cm. cells. In all cases the optical absorption increases continuously toward shorter wave lengths and the band maxima cannot be reached. Thus, as in the case of oxygen solutions,^{2,3} the band onset energy was used for the characterization of the absorption bands. We chose somewhat arbitrarily $\epsilon = 10$ mole⁻¹ liter cm.⁻¹ as the band onset. It is thus assumed that vibrational broadening is independent of the nature of the solvent. For charge transfer spectra of I₂ and O₂ this assumption was considered previously.^{3,12} The experimental results for NO solutions are presented in Table I.

Recently Drago and Piper⁸ reported absorption bands of NO in solutions of methanol and acetonitrile with an onset at about 385 m μ , characterized by a vibrational fine structure, extending to shorter wave lengths. These bands were assigned⁸ to spin forbidden transitions enhanced by the polar solvent. The band intensity reported for methanol¹³ $\epsilon \sim 50$ liter mole⁻¹ cm.⁻¹, is surprisingly high for a Laporte forbidden transition. Under our experimental conditions we were unable to observe the absorption bands reported by Piper and Drago in any of the solvents investigated by us. Careful scanning of the spectra (using a recording spectrophotometer) of NO in methanol and acetonitrile in the region 400–300 m μ did not show this transition. When the purification method of NO described by Drago¹³ was employed^{14a} we did in fact observe some unreproducible optical absorption in the region of 360 m μ . However when the nitric oxide was distilled *in vacuo* this absorption was no longer observed. We thus conclude that the band reported by Piper and Drago probably is due to impurities, presumably N₂O₃.

(12) J. Jortner and U. Sokolov, *Nature*, **190**, 1003 (1961).

(13) R. S. Drago, R. O. Ragsdale and D. P. Eyman, *J. Am. Chem. Soc.*, **83**, 4337 (1961).

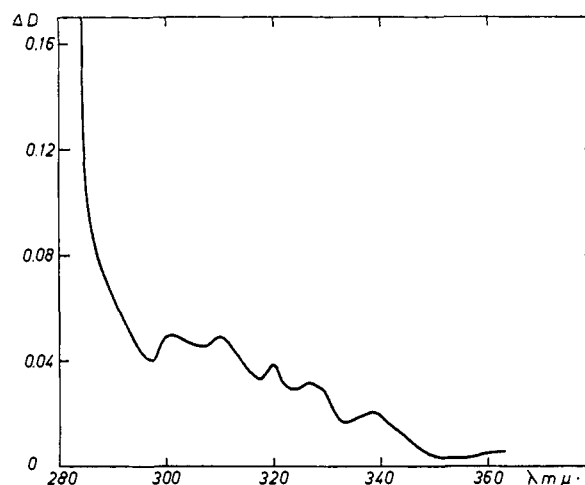


Fig. 2.—Singlet-triplet transition of benzene induced by NO: $P_{\text{NO}} = 350$ mm.; $l = 4.00$ cm.

Discussion

Nature of the Absorption Bands.—The absorption spectrum of gaseous NO is characterized by a set of sharp bands below 2300 Å. originating with the $\gamma(\text{O}-\text{O})$ band located at 227 m μ .^{10,11} Thus clearly the absorption bands of NO in solution are not due to allowed transitions of this molecule.

The absorption of NO in solution may be due to the spin forbidden transition $^2\text{II} \rightarrow ^4\text{II}$, which on a theoretical basis was predicted^{14b} to be located at 3.9 eV. However, we were unable to obtain any experimental evidence for this transition.

Another possible source of optical absorption of NO in solution may be dimerization of nitric oxide. Chemi-

(14) (a) In a private communication Professor Drago pointed out that the same purification method for NO was used in the work described in ref. 8, (b) H. Brion, C. Moser and M. Yamazaki, *J. Chem. Phys.*, **30**, 673 (1959).

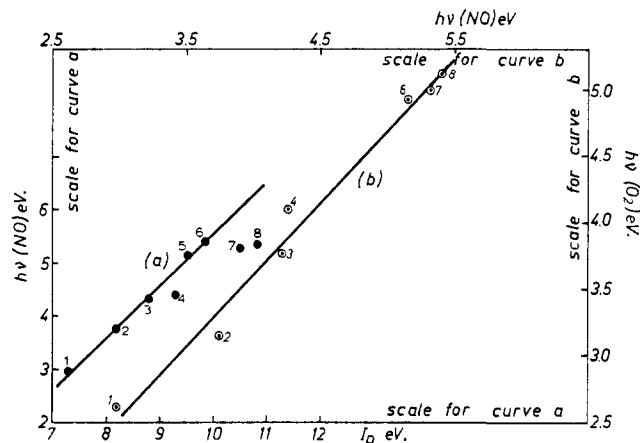


Fig. 3.—Energetic relationships for the charge transfer bands of NO in solutions: (a) The dependence of the equivalent energy of the band onset on the ionization potential of the solvent molecule. Ionization potentials from K. Watanabe, *J. Chem. Phys.*, 26, 542 (1952), and from ref. 2. (b) The relation between the equivalent band onset energies for the absorption spectra of nitric oxide and of oxygen in solution. Data for O₂ solutions from ref. 2 and 3. The signs for the donors are the same as in Table I.

cal and physical evidence^{15,16} indicates that liquid NO at low temperatures consists mainly of dimer molecules. The absorption spectra of liquid NO at -152° show two regions of strong absorption: one commencing at 400 $m\mu$ toward shorter wave lengths and the other at 560 $m\mu$ toward long wave lengths.¹⁷ The investigation of $\sim 0.3 M$ solutions of NO in liquid N₂ and liquid Kr¹⁶ and of NO in Ar and CO₂ matrices¹⁸ by infrared spectroscopy yields strong evidence for dimerization. The absorption bands for NO in solutions observed in the present work show no relationship to the spectral data reported by Bernstein and Herzberg.¹⁷ The ϵ values appear to be independent of NO pressure. These absorption spectra were observed at relatively low (10^{-2} – $10^{-3} M$) NO concentration at room temperature. It is known that at room temperature the association of gaseous NO to N₂O₂ is extremely small.¹⁹ Thus, we are impelled to conclude that the absorption bands observed under our experimental conditions are not due to nitric oxide dimers.

The weak absorption of NO in liquid benzene in the region 360–300 $m\mu$ is due to the first singlet–triplet transition ${}^1A_{1g} \rightarrow {}^3B_{1u}$ of benzene.^{1b,c} The band positions are in good agreement with the results obtained by Evans for this transition enhanced by O₂ and by NO.^{1b} The molar absorption coefficient (calculated using the NO concentration) for the O–O 340 $m\mu$ band is $\epsilon = 1.2$ liter mole⁻¹ cm.⁻¹.

The continuous diffuse bands of nitric oxide in solutions are more intense by a factor of 10^2 than the benzene singlet–triplet transition. These are attributed to charge transfer spectra, the NO molecule acting as an electron acceptor. The dependence of the position of the absorption bands on the nature of the solvent is reflected in the dependence of the equivalent energy of the band onset on the ionization potential of the solvent molecules (Fig. 3a). This correlation yields evidence for the identification of these absorption bands as arising from charge transfer absorption.

This linear plot is a consequence of Mulliken's charge transfer theory.²⁰ Theoretically

$$h\nu = I_p - E + \Delta + 2W^2/(I_p - E + \Delta) - U \quad (2)$$

(15) O. K. Rice, *J. Chem. Phys.*, 4, 367 (1936).

(16) L. Smith, W. E. Keller and H. L. Johnston, *ibid.*, 19, 189 (1951).

(17) H. J. Bernstein and G. Herzberg, *ibid.*, 15, 77 (1947).

(18) W. G. Fateley, H. A. Bent and B. Crawford, *ibid.*, 31, 204 (1961).

(19) H. L. Johnston and H. R. Weiner, *J. Am. Chem. Soc.*, 56, 625 (1934).

(20) R. R. Mulliken, *ibid.*, 74, 811 (1952).

where $h\nu$ is the equivalent energy of the band onset; I_p the vertical ionization potential of the electron donor; E is the vertical electron affinity of the electron acceptor (*i.e.*, NO); Δ is the stabilization energy of the excited state, relative to the ground state in the nuclear configuration of the ground state; W is the resonance integral between the ground state and the charge transfer state, while U represents the energy difference between band maximum and band onset. For weak complexes the term rising from second order perturbation energy can be neglected. If it is then assumed that Δ and U are constant for various electron donors a linear relationship between $h\nu$ and I_p is expected. Such relationships have been obtained previously for band maxima^{21–23} and band onsets^{2,3} of charge transfer spectra. The absence of a charge transfer band of NO in acetone is now understandable as the ionization potential 9.7 e.v. implies that the charge transfer band onset of NO should lie at about 250 $m\mu$ and thus, as in the case of O₂,² will be completely masked by the $n \rightarrow \pi^*$ transition of acetone.

It was frequently stressed²³ that the assumption that Δ is independent of the nature of the electron donor is not strictly justified. A more reasonable empirical approach will involve the comparison of spectroscopic data for one electron donor with two similar electron acceptors.¹² Δ is then expected to be constant for this pair. A similar assumption will involve the constancy of the corresponding U values for such a pair.¹² Thus we expect that the bands onset energies for one donor with O₂ and NO are related by

$$h\nu(\text{NO}) = h\nu(\text{O}_2) + E_{\text{O}_2} - E_{\text{NO}} \quad (3)$$

A plot of the experimental data obtained for NO in the present work and the data for the charge transfer bands of O₂ obtained previously^{2,3} is shown in Fig. 3b, yielding a further support to the assignment of the NO bands.

The absorption spectra of NO in water and in acetonitrile show a deviation from the regularities expected on the basis of the charge transfer theory. Comparing the band onsets for O₂ and NO in these two solvents the NO band onsets should be blue shifted to higher energy by about 0.5–1.0 e.v. It appears unlikely that the absorption observed in these solvents is due to the $\gamma(\text{O}-\text{O})$ transition located at 227 m .^{10,11} as this band is characterized by a relatively low molar absorption coefficient $\epsilon \sim 40$ liter mole⁻¹ cm.⁻¹,¹⁰ while as indicated by Fig. 1, the absorption of NO in water shows much higher ϵ values.

The Nature of the Interactions of NO with the Donor Molecules.—The interactions between NO and the solvent molecules investigated in this work appear to be very weak. The solubilities of NO do not decrease with the increase in the ionization potential of the solvent. Thus the Bunsen solubility coefficient of NO is 0.275 in benzene and 0.35 in methanol at 20°.³ From the temperature dependence of the solubility data⁹ of NO, ΔH for the solubility of NO was evaluated. For H₂O at 4°, $\Delta H(\text{NO}) = 4.6$ kcal. mole⁻¹, while for argon $\Delta H(\text{Ar}) = 3.73$ kcal. mole⁻¹. For benzene at 20°, $\Delta H(\text{NO}) = -0.35$ kcal. mole⁻¹, while $\Delta H(\text{N}_2) = 0.86$ kcal. mole⁻¹. It appears that no thermochemical evidence is obtained for complex formations in these NO solutions. Thus the solubility of NO is determined by the structure of the solvent and charge transfer interactions do not contribute appreciably to the heat of solution. This situation is similar to that in O₂ solutions.³ The continuous bands of NO should be thus assigned to contact charge transfer.⁷

(21) G. H. Hastings, J. L. Franklin, J. C. Schiller and F. A. Matsen, *ibid.*, 75, 2900 (1953).

(22) S. Briegleb and J. Czekała, *Z. angew. Chem.*, 72, 401 (1960).

(23) R. S. McGlynn, *Chem. Revs.*, 58, 1113 (1958).

An Estimation of the Electron Affinity of NO.—It was pointed out recently that energetic data from charge transfer spectra may be useful for the calculation of vertical electron affinities of some diatomic molecules.¹² The electron affinity of NO is unknown; however, electron attachment experiments indicate that it is positive.²⁴ From the comparison of the charge transfer spectra of NO and O₂,^{2,5} it follows from equation 3 that for eight donors (excluding acetonitrile and water) $E_{O_2} - E_{NO} = 0.36 \pm 0.15$ e.v.

The electron affinity of O₂ was determined recently from charge transfer spectra¹² to be $E_{O_2} = 0.78 \pm 0.1$ e.v. This value is in good agreement with thermochemical data²⁴ but is higher than the value 0.15 e.v. determined by Mulliken from theoretical considerations.²⁵ Recently the value of 0.46 e.v. for E_{O_2} was reported.²⁶ If O₂ were in an excited state in the above-mentioned collisional detachment experiments,²⁶ E_{O_2} would be about 0.9 e.v. Using the value of E_{O_2} from charge transfer spectra,¹² it follows that $E_{NO} = 0.42 \pm 0.2$ e.v. If the value for E_{O_2} obtained by Phelps and Pack²⁶ were used, then it follows that the electron affinity of NO is nearly zero. However, independent experimental evidence shows that the electron affinity of NO is positive. In solutions of N₂O in water, methanol and dimethylaniline no charge transfer bands due to the interaction of N₂O with the solvent could be observed.²⁷ Mass spectrometric experiments show that the electron affinity of N₂O is nearly zero^{28,29} as electron capture by N₂O leads to dissociation to N₂ + O⁻ with a threshold energy of less than 0.05 e.v. Thus we are impelled to conclude that the charge transfer absorption bands of N₂O in solution (if they exist at all) are blue shifted compared to those of NO and thus $E_{NO} > E_{N_2O}$.

It appears that the value of 0.4 e.v. for E_{NO} is reasonable. This result furnishes a further example for the usefulness of spectroscopic results for the derivation of energetic data.

The Energy Levels of the D-NO Contact Pairs.

The theoretical treatment of the absorption bands induced by NO in solution is a straightforward extension of the theoretical treatments due to Tsubomura and Mulliken,² Hoijtink⁵ and Murrel.⁶ In Fig. 4 the low-lying energy levels of the donor molecule and of the NO molecule are shown. The ground state of NO is a ${}^2\Pi_{3/2}$ state with one unpaired electron in the doubly degenerate π_g m.o. The ground state of D is assumed to be a totally symmetric 1A singlet state. Hence the over-all ground state of the D-NO pair produced by "contacts" of the donor and NO molecules is a doublet state. The excited singlet 1E and triplet 3E states of the isolated donor lead to 4F , 2F and 2G states (Fig. 4). The charge transfer state is due to electron transfer from the highest filled m.o. of D, $\phi(D)$, to a π_g NO orbital leading to doublet and quartet states, since NO⁻ is in a triplet and D⁺ is in a doublet state. The following transitions of the D-NO pair are thus expected: ${}^2A \rightarrow {}^2F$; ${}^2A \rightarrow {}^2CT$ and ${}^2A \rightarrow {}^2G$.

The intensity of the charge transfer transition ${}^2A \rightarrow {}^2CT$ for these contact charge transfer complexes is mainly due to interaction between the 2CT and the 2G excited state.^{2,30} Intensity is borrowed from the nearest strongly allowed transition of the donor. The

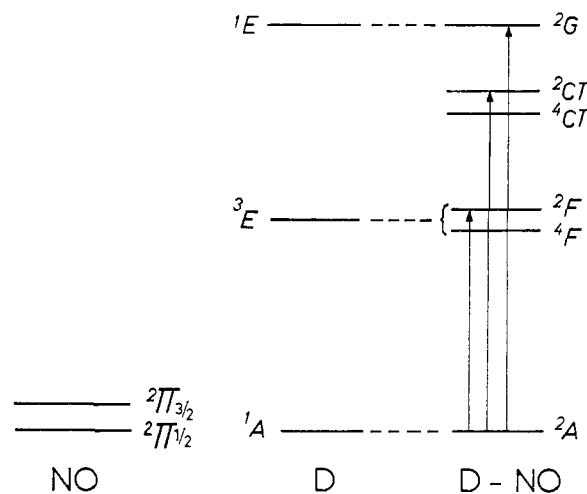
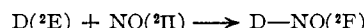


Fig. 4.—Schematic diagram of the energy levels for a NO molecule, a donor molecule and their contact pair.

${}^2A \rightarrow {}^2CT$ band borrows $(\beta/\Delta E)^2$ from the ${}^2A \rightarrow {}^2G$ band intensity,² where β is the resonance integral between the 2CT and the 2G states. It is reasonable to expect that the resonance integrals β for the pairs D-NO and D-O₂ will be about equal, as in the one-electron approximation both are determined by the overlap distribution $\pi_g\phi(D)$ in the core potential of D⁺.⁶ Thus the intensities of the contact charge transfer bands of NO and O₂ are expected to be about equal.

The ${}^2A \rightarrow {}^2F$ transition, which is equivalent to the singlet-triplet transition of the isolated donor molecule, is now spin allowed. However, as Tsubomura and Mulliken have shown² configuration interaction is required to account for the intensity of this transition. As in the case of O₂, the interaction between the 2F and 2G states^{2,5} is probably less important than between the 2F and 2CT states. Again, the resonance integrals for the perturbation of the F state by the CT state for NO and O₂ are expected to be about equal, as they are mainly determined by the overlap distribution $\pi_g\phi(D)$ in the core potential of the neutral acceptor.⁶ The intensity of the enhanced singlet triplet transition of benzene induced by NO has an intensity comparable to the O₂ enhanced transition. For the 340 m μ O-O band $\epsilon = 1.2$ liter mole⁻¹ cm.⁻¹ in NO solution and $\epsilon \sim 1$ liter mole⁻¹ cm.⁻¹ for O₂ solutions.^{2,16} This result is in agreement with the theoretical expectation.

Triplet-State Quenching by NO.—The charge transfer spectra of NO observed in the present work are relevant for the quenching mechanism of triplet states by nitric oxide. A quenching mechanism based on the role of charge transfer states was recently considered by Linschitz and Pekkarinen.³¹ The quenching of a triplet state by NO will involve the formation of a contact pair between the excited molecule in the triplet state and NO



followed by the internal conversions ${}^2F \rightarrow {}^2CT \rightarrow {}^2A$. The results of Porter and Wright³² lead to a rate constant of 4×10^9 M⁻¹ sec.⁻¹ for the quenching of the triplet state of anthracene by NO in hexane solution, which is practically identical with the quenching rate constant by O₂ in this system.³² The quenching mechanism of a triplet state by NO or O₂ via a charge transfer state has to take into account the energies of the F, CT and A states as a function of the D-NO

(24) H. O. Pritchard, *Chem. Revs.*, **52**, 529 (1953).

(25) R. S. Mulliken, *Phys. Rev.*, **115**, 1225 (1959).

(26) A. H. Phelps and J. L. Pack, *Phys. Rev. Letters*, **6**, 111 (1961).

(27) R. Grajower and J. Jortner, unpublished results. In H₂O and methanol an absorption was observed which is due to the tail of the 1840 Å. band of N₂O.

(28) G. J. Schulz, *J. Chem. Phys.*, **34**, 1778 (1960).

(29) R. D. Curran and R. B. Fox, *ibid.*, **34**, 1590 (1960).

(30) J. N. Murrel, *J. Am. Chem. Soc.*, **81**, 5037 (1958).

(31) H. Linschitz and L. Pekkarinen, *ibid.*, **82**, 2411 (1960).

(32) G. Porter and H. R. Wright, *J. chim. phys.*, **55**, 705 (1958).

or D-O₂ separations.³¹ When the quenching efficiencies of O₂ and NO are compared, as the interactions in the A and F states are weak, the change of the acceptor will mainly affect the charge transfer state. As E_{NO} is lower than E_{O_2} , the potential curve for the C·T state of D-NO will lie about 0.4 e.v. higher

than that for the D-O₂ pair. The results of Porter and Wright³² indicate that in spite of the rise in the C·T state potential curve, the $^3F \rightarrow ^3CT$ radiationless transitions for NO quenching are not activation controlled, proceeding at every encounter as in the case for the $^3F \rightarrow ^3CT$ radiationless transitions for O₂ quenching.

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Substituent Effects on Nuclear Magnetic Resonance Coupling Constants and Chemical Shifts in a Saturated System: Hexachlorobicyclo[2.2.1]heptenes¹

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RECEIVED AUGUST 30, 1962

The coupling constants between protons on adjacent saturated carbon atoms have been found to depend on the electronegativity of the substituent adjacent to the coupling protons in a series of monosubstituted hexachlorobicyclo[2.2.1]heptenes. Assuming a \cos^2 dependence of the coupling constant on dihedral angle, these coupling constants are shown to be remarkably similar to those observed for the corresponding ethylene compounds. The internal chemical shifts, $\delta_X - \delta_A$ and $\delta_X - \delta_B$ between the X and A or B protons in this rigid ABX system have been found to depend on both the electronegativity of the substituent and on the dihedral angle between the CX bond and those bonds involving the adjacent (A or B) protons.

Introduction

The purpose of the work reported herein was to determine the effect of various substituents on the coupling constants between protons on adjacent carbon atoms in a rigid saturated system. Karplus has demonstrated theoretically that the coupling constants of protons on adjacent carbon atoms are functions of the dihedral angles between the protons governed by the relationship²

$$J = \begin{cases} 8.5 \cos^2\phi - 0.28, & 0^\circ \leq \phi \leq 90^\circ \\ 9.5 \cos^2\phi - 0.28, & 90^\circ \leq \phi \leq 180^\circ \end{cases}$$

This relationship has been shown experimentally to apply to a wide variety of compounds³ with varying degrees of precision.

In an analysis of the X portion of the ABX system found in six isomeric α -acetoxy ketones in the A-ring of a steroid, we found it necessary to revise the constants of the Karplus equation in order to obtain mutually consistent values for the dihedral angles between the coupling protons in these compounds.⁴ It is not surprising, in view of the approximations involved in Karplus' theoretical calculations, that such a revision should be necessary. However, our revised equation did not give mutually consistent values for calculated dihedral angles when applied to similar compounds with different substituents adjacent to the coupling protons.⁴ In short, the magnitude of the observed coupling constants in this system seemed to vary, not according to changes in the dihedral angle between the coupling protons, but according to the nature of the substituent adjacent to the coupling protons. In view of the conformational flexibility of the A-ring of the steroid molecule such a conclusion must, of necessity, be regarded as tenuous. Furthermore because the

AB lines of the ABX pattern are not clearly resolved from the lines due to the many other protons in the molecule, a complete ABX analysis is impossible.

Substituent effects on the couplings between protons on saturated carbon atoms have been remarked upon by previous workers. In a study of some cyclopropane carboxylic acids, Hutton and Schaefer^{5f} indicated that the difference between their observed coupling constants and those calculated from the Karplus equation may depend on the electronegativity of the substituent, although they did not rule out distortion of the ring system by the large substituents. By way of contrast Graham and Rogers⁵ in a recent study of a series of cyclopropane derivatives, including some cyclopropanecarboxylic acids, concluded that substituent effects were not important in the consideration of the proton-proton coupling constants.

The observed⁶ coupling constants in three-membered rings containing the heteroatoms oxygen, nitrogen, and sulfur do not agree well with Karplus' predictions. Hutton and Schaefer^{5f} again noted that the deviations from the predicted values parallel the differences in electronegativity between the heteroatoms and carbon, from which they conclude that the coupling constants in these heterocyclic compounds depend not only on angular factors but also on the electronegativity of the heteroatom.

The Hexachlorobicyclo[2.2.1]heptene System.—In order to determine the effect of substituents of varying electronegativity and magnetic anisotropy on the magnitude of the coupling constant between protons on adjacent saturated carbon atoms, it is necessary to have a system in which the stereochemistry of the coupling protons remains fixed and known. Only in this way can the effect of the substituent on the coupling constant be separated from the known dependence^{2,3} of J on the dihedral angle between the coupling protons. Furthermore the system must have a minimum number of coupling protons to facilitate complete, unambiguous analysis of the spectra and, finally, it must be possible to introduce a variety of groups of differing magnetic anisotropy and electronegativity. For these reasons we have chosen to examine the n.m.r. spectra of Diels-Alder adducts formed from hexachlorocyclopentadiene and a series of monosubstituted ethylenes.

(1) This work was presented at the 142nd Natl. Meeting of the American Chemical Society at Atlantic City, N. J., September, 1962. This investigation was supported in part by PHS research grant GM 10224-01 from the Division of General Medical Sciences.

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