[CONTRIBUTION NO. 477 FROM THE INSTITUTE FOR ATOMIC RESEARCH AND DEPARTMENT OF CHEMISTRY, IOWA STATE COLLEGE]

Regularities in the Infrared Spectra of Picric Acid Molecular Complexes[1]

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The infrared spectra of forty picric acid molecular complexes show that the nitro asymmetric stretching and the out-of-plane C–H bending vibrations of the picric acid component are sensitive to complex formation. The frequencies of these vibrations can be correlated with the type of complex formed, *i.e.*, π-π or n-π type charge transfer. Many of the complexes were found to contain an additional asymmetric nitro stretching vibration. The appearance of this additional band and independent crystallographic evidence suggest that these particular complexes contain an additional localized intermolecular interaction.

I. Introduction

The existence of molecular complexes between nitro-substituted benzenes and aromatic hydrocarbons has long been recognized. Many theories have been advanced to explain the nature of these complexes but only recently has one been proposed which is completely acceptable. This theory is found in a series of papers by Mulliken[3] whose general quantum-mechanical treatment of molecular complexes encompassed all of the preceding major, classical theories.[3,4] Mulliken suggested that the formation of molecular complexes from two aromatic molecules can arise from the transfer of an electron from a π-molecular orbital of a Lewis base to a vacant π-molecular orbital of a Lewis acid, with resonance between this dative structure and the no-bond structure stabilizing the complex. He also noted the possibility of complex formation through the donation of an electron from a nonbonding molecular orbital in a Lewis base to a vacant π-orbital of an acceptor (n-π interaction),[3b] with resonance stabilization of the combination.

Mulliken's ideas have been supported by spectroscopic evidence. The dichroism studies by Nakamoto[5] of molecular complexes of a type similar to those treated in this paper clearly indicate the existence of charge transfer forces operating between the two components of the complex. The original attraction of the two components, according to Nakamoto, arose from mutual polarizing forces which caused attracting dipoles. When the two molecules approached each other closely enough so as to be in the effective π-electron fields of each other, the electron transfer could then occur.

The intermolecular charge transfer predicted by Mulliken gives rise to intense electronic absorption bands in many complexes. These bands were examined by McConnell, *et al.*,[6] and Hastings, *et al.*,[7] who used them to set up empirical methods which would predict the wave lengths and intensities of these charge transfer absorptions.

Whereas the ultraviolet region can be used to study the electronic characteristics of these complexes, the infrared spectra can be utilized to examine the result of the charge transfers. Since the stability of these complexes arises from a shift of electron density from the donor to the electron deficient acceptor molecule, the infrared region should record the effect of the change of electron density in the components upon the vibrations of the atoms within the individual molecules. Study of vibrational spectra may also reveal which parts of the molecules play an active role in complex formation.

II. Experimental

The forty picric acid complexes listed in Table I were studied in Nujol (mineral oil) mulls with a Perkin–Elmer Model 13 Infrared Spectrophotometer, using sodium chloride optics. Approximately half of the complexes were prepared by the authors using a number of different methods, depending upon the individual compound. Many were crystallized from a hot saturated solution of picric acid in ethanol or chloroform to which was added the second component. In other cases where the latter component was a liquid, the picric acid was added directly to the hot liquid and the excess solvent evaporated under reduced pressure. The complexes which were not prepared by us were obtained from the Iowa State College Chemistry Department.

III. Experimental Results

In general, the spectra of all the molecular complexes appear to be a summation of the spectra of the two components, with the vibrational bands of picric acid appearing more strongly than those of the other components. Because of the large differences in the spectra of the various hydrocarbon (Lewis base) components of the complexes, it was difficult to uncover any systematic spectral changes in their spectra when complexes were formed. For this reason, emphasis was placed on noting whether any significant changes occurred in the spectra of the picric acid component. In the wave length region investigated only the nitro asymmetric stretching vibrations and the C–H out-of-plane bending vibrations of the picric acid component showed significant changes.

These frequency changes are not simple in nature as shown by the summary of data in Table I. Both the nitro asymmetric stretching and the C–H out-of-plane bending vibrations exhibit frequencies less than, approximately equal to, or greater than the corresponding frequencies in picric acid. An additional nitro asymmetric stretching vibration also appears in most of the complexes. The frequency of the symmetric nitro stretching vibration shows much smaller variations

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(1) Work was performed in the Ames Laboratory of the Atomic Energy Commission.

(2) Rayonier Incorporated, Whippany, New Jersey.

(3) (a) R. S. Mulliken, THIS JOURNAL, **72**, 600 (1950); (b) **74**, 811 (1952); (c) *J. Phys. Chem.*, **56**, 801 (1952).

(4) (a) J. Weiss, *J. Chem. Soc.*, 245 (1942); (b) W. Brackmann, *Rec. trav. chim.*, **68**, 147 (1949); (c) M. J. S. Dewar, *Nature*, **156**, 784 (1945); *J. Chem. Soc.*, 406, 777 (1946).

(5) K. Nakamoto, THIS JOURNAL, **74**, 1739 (1952).

(6) H. McConnell, J. S. Ham and J. R. Platt, *J. Chem. Phys.*, **21**, 66 (1953).

(7) S. H. Hastings, J. L. Franklin, J. C. Schiller and F. A. Matsen, THIS JOURNAL, **75**, 2900 (1953)

TABLE I

No.	Compd. complexed with picric acid	Frequency of nitro asymmetric stretching vibration (cm.$^{-1}$) Normal	"Bonded"	C-H out-of-plane bending frequency (cm.$^{-1}$)	Type of complex
1	Mesitylene	1526	..	780.6	π-π
2	Fluorene	1528	..	783.1	π-π
3	Indene	1528	..	Overlap	π-π
4	Phenanthrene	1534	..	780.0	π-π
5	Tetralin	1539	..	780.6	π-π
6	Naphthalene	1541	..	779.0	π-π
7	Anthracene	1542	..	777.7	π-π
8	Hexamethylbenzene	1543	..	783.1	π-π
9	Anisole	1524	1514	783.8	π-π
10	Aniline	1525	1491	792.1	π-π
11	Phenetole	1526	1508	783.0	π-π
12	*p*-Iodoaniline	1531	1513	789.1	π-π
13	β-Naphthylamine	1536	1521	792.5	π-π
14	β-Naphthol	1536	1507	780.4	π-π
15	β-Naphthyl ethyl ether	1536	1507	779.6	π-π
16	α-Naphthyl methyl ether	1537	1504	779.5	π-π
17	β-Methylnaphthalene	1537	1504	779.4	π-π
18	2-Aminodibenzofuran	1540	1525	785.7	π-π
19	β-Naphthyl methyl ether	1542	1507	779.5	π-π
20	Guaiacol	1542	1513	783.1	π-π
21	α-Benzylpyrroline	1530	1549	785.4	n-π
22	Strychnine	1506	1523	787.8	n-π
23	Pyridine	1506 1520	1548	786.0	n-π
24	α-(*p*-Tolyl)-pyrroline	1513	1551	787.4	n-π
25	Atropine	1515	1560	787.5	n-π
26	β-Picolylamine	1515	1540	792.2	n-π
27	4,7-Dichloroquinoline	1520	1536	789.3	n-π
28	7-Chloro-4-(N-morpholino-amino)-quinoline	1520	1548	789.7	n-π
29	α-(*p*-Tolyl)-pyrrolidine	1523	1545	791.3	n-π
30	Piperidine	1524	1548	786.9	n-π
31	α-Ethylpyrroline	1525	1543	789.7	n-π
32	α-(*p*-Chlorophenyl)-tetrahydropyridine	1526	1546	787.0	n-π
33	α-Phenylpyrroline	1528	1535	789.8	n-π
34	Nicotine	1529	1543	787.4	n-π
35	β-(*p*-Tolyl)-tetrahydropyridine	1532	1541	786.6	n-π
36	Tetramethylpyrazine	1536	1540	788.0	n-π
37	N-(*p*-Tolyl)-pyrrolidine	*a*	1548	787.3	n-π
38	*o*-Phenanthroline	1545	..	784.9	π-π
39	α-(α-Naphthyl)-pyrroline	1532	1508 1548	780.2 790.6	π-π n-π
40	2,3-Diaminobutane	1514	1541	793.7	h.b.[b]
	Picric acid	1525	..	783.3	..

[a] Peak frequency masked. [b] Hydrogen bonded complex.

from complex to complex, and in cases where the asymmetric band is split into two components, the symmetric vibration at most shows a slight broadening.

IV. Discussion

Before discussing the spectra of specific complexes it is advisable to consider the nitro asymmetric stretching vibrations in picric acid itself. Picric acid contains three nitro groups whose stretching frequencies are not expected to be equivalent. One nitro group *ortho* to the phenolic OH is involved in a hydrogen bond with that group. As a result of this interaction, the asymmetric stretching frequency of the nitro group is decreased. The other, non-bonded, *ortho* nitro group is rotated out of the plane of the ring because of the steric effect of the OH group. The *para*-nitro group is coplanar with the ring, as is one *ortho*-nitro group, but it is not involved in an intramolecular hydrogen bond. The three nitro asymmetric stretching frequencies are not resolved, and appear as one broad band with a maximum at 1525 cm.$^{-1}$ (Fig. 1A). The remainder of Fig. 1 shows the nitro asymmetric frequencies in some typical picrate complexes.

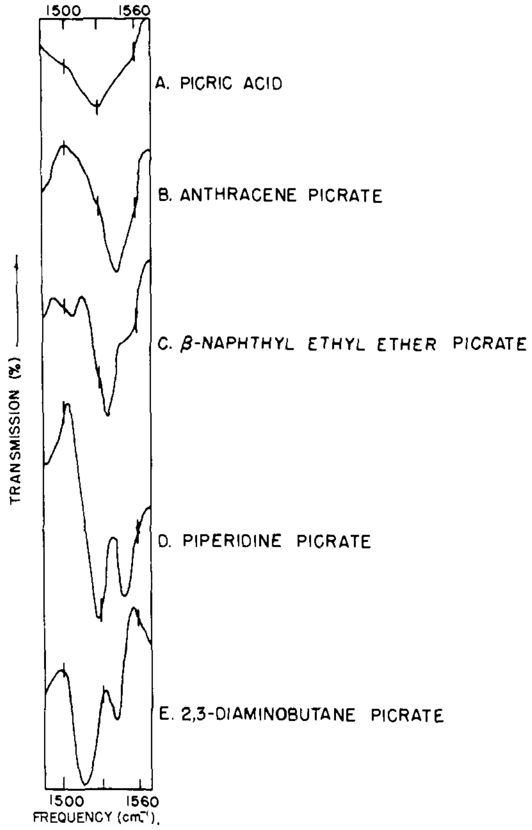

Fig. 1.—Nitro asymmetric stretching absorption bands in picric acid and picrate complexes. Spectra were obtained from Nujol mulls of the crystals.

At first glance the nitro asymmetric stretching and the C–H out-of-plane bending frequencies of the forty complexes appear to vary in a complex manner. However, on the basis of certain consistencies among these frequencies, there is a possibility of classifying the complexes into three general groups. This classification is reinforced by the significant similarities among the electron donor molecules in each group.

Group I.—This group is comprised of complexes formed with compounds numbered 1–8 in Table I. All of these complexes show a single broad nitro band, greater in frequency than that for picric acid. In addition, the corresponding C–H out-of-plane frequencies are all lower than in picric acid. With the exception of compounds 1 and 8, the donor molecules in this group of complexes are all unsubstituted polynuclear aromatics which are expected to form typical π-π complexes. These complexes are therefore classified as π-π type in Table I.

Group II.—The spectra of complexes formed from compounds numbered 9–20 all show two nitro asymmetric stretching frequencies. One of these is again equal to or greater than the frequency of the single band found in picric acid; the additional band is located at considerably lower frequencies. The C–H out-of-plane bending frequencies scatter rather uniformly around the 783.3 cm.$^{-1}$ frequency of picric acid. A characteristic possessed by all complexes showing the extra band is that the hydrocarbon (Lewis base) component contains an electron donating group (OH, CH_3, NH_2, etc.). Moreover, the relative intensity of this extra band varies directly with the basic strength (in the Lewis sense) of the electron donating substituent on the donor molecule. This relationship is illustrated (Fig. 2) in the spectra of four β-substituted naphthalenes. It is seen that the relative intensity increases in the order CH_3, OCH_3, OH, NH_2.

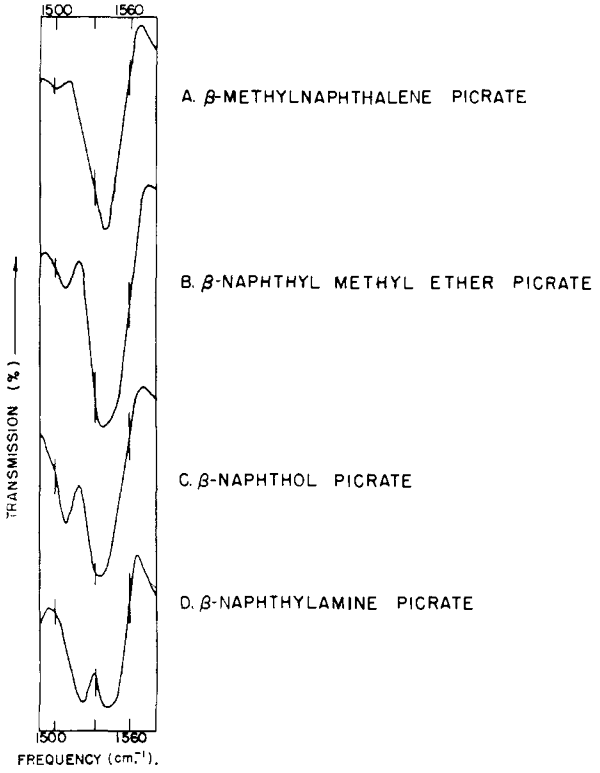

Fig. 2.—Intensity variations of additional nitro stretching band in π-π complexes. Spectra were obtained from Nujol mulls of the crystals.

Although these compounds would be expected to form typical π-π complexes, the appearance of the additional nitro band as well as independent evidence obtained by others suggests the existence of a localized intermolecular interaction in addition to the general charge transfer between delocalized π-orbitals of the aromatic nuclei. Powell, *et al.*,[8] have found from crystal structure data on the π-complex of *p*-iodoaniline and *sym*-trinitrobenzene, that one nitro group approaches the ring of *p*-iodoaniline more closely than do the other two. The approach distance is smaller than that usually associated with van der Waals forces. Significantly, this complex shows the additional nitro asymmetric stretching frequency found in this group of picric acid complexes.

The spectroscopic and crystallographic considerations outlined above are suggestive of a localized interaction between the electron donating group on the donor and one of the nitro groups on the acceptor molecule. The reasons for the apparent decrease in the asymmetric stretching frequency of the specific nitro group involved in the interaction, and the changes in relative intensity with the donor group basicity appear to be too complex to provide conclusive evidence for this localized interaction.

Group III.—The spectra of the complexes in this group, 21–37, exhibit two nitro asymmetric stretching vibrations, one stronger than the other. The more intense band is located in the region in which the nitro vibration is found in picric acid, and the weaker band is found at considerably higher frequencies (around 1545 cm.$^{-1}$) (Table I and Fig. 1D). The C–H out-of-plane bending vibrations invariably appear at a higher frequency than in pure picric acid. A characteristic common to all of the complexes in this group is that the donor molecule contains an atom which permits it to act as an n-base and form strong localized n-π complexes. The charge transfer takes place between a non-bonding orbital of the heterocyclic nitrogen atom and a vacant orbital of one of the nitro groups. These considerations lead to the classification of these structures as n-π complexes (Table I).

For purely localized n-π intermolecular interactions, a reaction-site to reaction-site approach of the two molecules is preferred to the parallel arrangement of π-π complexes. This leads to a closer proximity of the two interacting orbitals and hence greater interaction stability. The overall effect of this localized charge transfer is a significant increase in the asymmetric stretching vibration of the nitro group involved in the interaction.

V. Complexes Showing Noteworthy Behavior

***o*-Phenanthroline Picrate (No. 38).**—The heterocyclic nitrogen atoms in *o*-phenanthroline should lead to the formation of an n-π complex, but the appearance of only a single nitro asymmetric stretching vibration indicates that a π-π complex is formed. In this compound steric factors may be inhibiting the formation of an n-π complex in favor of a π-π complex.

α-(α-Naphthyl)-pyrroline Picrate (No. 39).—The spectrum of this complex indicates two types of nitro and C–H band systems, the frequencies of one characteristic of predominantly π-π bonding and the frequencies of the other suggestive of n-π bonding. Consideration of the structure of the donor compound clearly indicates the possibility

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[8] H. M. Powell, G. Huse and P. W. Cooke, *J. Chem. Soc.*, 153 (1943).

for the formation of both types of complex; the naphthalene ring provides a site for π-π bonding and the nitrogen of the pyrroline possesses an electron which can be donated to an accepting orbital of a nitro group to form an n-π bond. Because of steric factors, a single donor molecule will probably have only one picric acid molecule associated with it, either in a π-π or an n-π bond.

2,3-Diaminobutane Picrate (No. 40).—In the spectrum of the 2,3-diaminobutane–picric acid complex, the pronounced shift of the NH_2 stretching vibrations to lower frequencies (3420 to 3207 cm.$^{-1}$) clearly indicates that the product is stabilized by hydrogen bonds between the amino hydrogens of one component and the nitro oxygens of the other. There are other cases where hydrogen bonding may further stabilize already formed π-π and n-π complexes, as in the picrates of aniline, β-naphthylamine and piperidine.

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The Application of Differential Thermal Analysis to the Study of Reaction Kinetics[1]

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Equations are derived which relate the shape of a differential thermal analysis curve to the kinetics of the reaction giving rise to the curve. For certain reactions, use of these equations allows the order of the reaction, the frequency factor, the activation energy and the heat of reaction to be determined in a single rapid measurement. The equations are applied to the decomposition of benzenediazonium chloride and the reaction between dimethylaniline and ethyl iodide. The results agree very well with data obtained by conventional methods.

Increasing use has been made of differential thermal analysis (DTA) in recent years for studying the processes which a substance undergoes on heating.[2] The differential thermograph is commonly used to determine if a reaction or transition occurs and the temperature at which it takes place. The present article shows that the kinetic parameters for the reaction giving rise to the DTA curve can be accurately determined by an analysis of the shape (*i.e.*, slope, height, area) of the curve. Conditions are assumed in the derivation which can be met more readily by liquids than by solids. The present discussion will therefore concern itself primarily with reactions occurring in solution.

Theory

The apparatus referred to in this derivation is shown in Fig. 1. It consists of two cells mounted in a bath. One cell contains the solution of reactants and the other pure solvent or other inert liquid. The contents of the cells are agitated by the indicated stirrers. The temperature of the bath is raised by a heater (not shown). The temperature of the reactant solution as well as the temperature difference between the contents of the two cells (ΔT) is measured as a function of time. A differential thermocouple (DTC) may be used to measure ΔT. The run is started at a sufficiently low temperature so that the reaction is not occurring at an appreciable rate and it is carried through until the reaction has gone essentially to completion. A curve such as the one in Fig. 2 is obtained.

T_1, T_2 and T_3 are the temperatures of the reactant solution, the liquid in the reference cell and the bath, respectively. $C_{p,r}$ is the total heat capacity of the reactant solution and $C_{p,s}$ the total heat capacity of the liquid in the reference cell.

We first set up the equations of heat balance (eq. 1 and 2). Equation 1 states that the increase in the enthalpy of the reactant solution ($C_{p,r}\, dT_1$) is equal to the heat evolved by the reaction (dH) plus the heat transferred into the cell from the surroundings.

$$C_{p,r}\, dT_1 = dH + K_r(T_3 - T_1)dt \qquad (1)$$

K_r is the heat transfer coefficient of the reactant cell and dt the time interval. Similarly for the liquid in the reference cell we have

$$C_{p,s}\, dT_2 = K_s(T_3 - T_2)dt \qquad (2)$$

where K_s is the heat transfer coefficient of the reference cell.

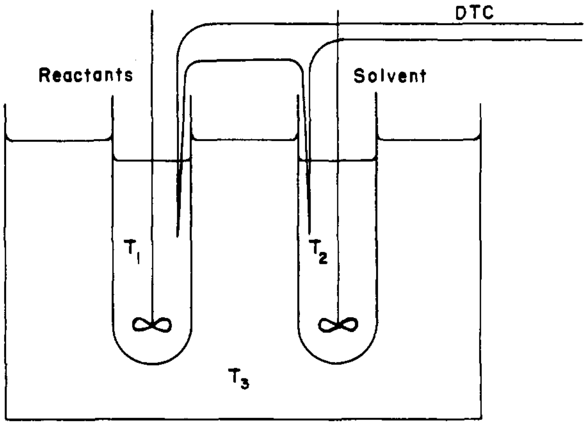

Fig. 1.—DTA apparatus for obtaining kinetic data for reactions occurring in solution.

Thus far two assumptions have been made. The first is that the temperature in the respective cells is uniform. This assumption was made when a single value of the temperature (T_1 and T_2) was assigned to the liquids in the cell. The condition

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[1] Presented in part at the 129th meeting of the American Chemical Society, Dallas, Texas, April, 1956. Further details may be found in a Ph.D. thesis by Hans J. Borchardt, filed with the Library of the University of Wisconsin, June, 1956.

[2] For an introduction to differential thermal analysis see H. J. Borchardt, *J. Chem. Ed.*, **33**, 103 (1956).