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Diphenylamine as an *n* and π Donor in the Solid-State Reaction of 2,4-Dinitrotoluene with Diphenylamine

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The kinetics and mechanism of the reaction of 2,4-dinitrotoluene with diphenylamine were studied in the solid state. The reaction product is a charge transfer complex with a localized intermolecular interaction as shown by uv and ir spectroscopy. The solid-state studies were complemented by some NMR studies in CCl_4. A novel feature of the study reveals that diphenylamine in this case is a much more powerful *n* donor than a π donor.

Introduction

The interest in the reactions of organic solids is of recent origin. In fact a book (*1*) on solid-state chemistry published in 1976 does not refer to any organic reaction in its chapter on chemical reactions. Similarly a review on solid-state chemistry by Cohen and Green (*2*) in 1973 refers to very few organic solid-state reactions.

Charge transfer complexes are finding an increasing importance in the area of organic solid-state chemistry due to their potential uses as organic metals (*3*). The enthalpy of formation is usually less negative than -10 kcal $mole^{-1}$ (*4*). And hence in some cases when the acceptor or the donor is very weak they may be normally difficult to isolate. However, even in such cases the Rastogi technique can give useful results.

There has been some controversy regarding the role of aromatic amines, i.e., whether they behave as *n* donors or as π donors. Though studies have been largely inconclusive there is now generally a broad agreement that they act as *n* donors toward σ acceptors like iodine and as π donors toward π acceptors such as sym-trinitrobenzene (*5*). There is only one study where evidence is adduced to show that in some systems both types of donation may operate simultaneously (*6*). Our present study is in line with this view. However, we depart from presently held notions (*7*) and give evidence to show that diphenylamine (DPA) is a much more powerful *n* donor than a π donor toward 2,4-dinitrotoluene (DNT), which is a π acceptor.

Experimental

Materials. DNT (Fluka) and DPA (B.D.H. Analar) were used after crystallization to constant melting point. CCl_4 (B.D.H. Analar) was used as is. Cyclohexane (Riedel, spectroscopic grade) was also used as is. To obtain a substance in a defi-

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nite particle size it was ground in a mortar and sized with standard sieves.

Apparatus. Graduated capillaries (10 cm long with an internal diameter of 0.3 cm.), Cook's M 400 series research microscope, Bausch and Lomb Spectronic 600 and 710, and Varian 60 D were used for kinetic studies, particle size measurements, infrared spectra, reflectance spectra, and NMR studies, respectively.

Kinetics. The kinetics of the solid state was studied by the capillary method developed by Rastogi *et al.* (*8*), using DNT (100–200 μm) and DPA (50–100 μm) particle sizes. The substances were packed in the capillary with the help of two iron rods by applying, as far as possible, uniform pressure as described earlier (*9*). The reaction rate was followed in an electrically controlled oven at the desired temperatures. A yellow-colored boundary, formed at the junction of the reacting substances, moved toward the reagent (DNT). The distance through which the colored boundary moved was noted to +0.01 cm and the accuracy and precision of the kinetic data were found to be 3 to 4%. The kinetic studies were made at different temperatures and for particles of various mesh sizes (i) below 50, (ii) 50–100, and (iii) 100–200 μm for DPA.

Spectroscopic studies. Reflectance spectra of the reactants and the products obtained by intimately mixing the reactants in different mole ratios in the solid state were recorded. Infrared spectra were likewise obtained by the KBr disk technique. The uv spectra in solution were obtained in two sets. The spectra between 200 and 300 nm were recorded in cyclohexane and the spectra from 300–700 nm were recorded in carbon tetrachloride.

NMR studies. The studies were carried out in CCl_4 solutions. A saturated solution of DNT was approximately 0.165 *M*. DPA was fairly soluble. For association constant studies it was found to be difficult to prepare the sample solution by mixing the solutions of DNT and DPA in the required ratio. A technique was therefore developed. DNT and DPA were mixed in the required ratio in the solid state and then dissolved in CCl_4. This device succeeded in giving solutions with a high donor/acceptor ratio and yet the concentration was such that good NMR signals could be obtained. The "a" protons of DNT (see the tables) merged with the signals of the aromatic protons of DPA at the concentrations used for the evaluation of K^{AD}.

Association constants. These were evaluated in solution both by visible and NMR spectrometry. The method of determination was that of Benesi and Hildebrand, as described by Foster in Ref. (*19*), for the visible and that of Hanna and Ashbaugh (*10*) for NMR.

Results and Discussion

DNT is an unusual acceptor in many ways. The electron-releasing effect of the CH_3 group compensates partly for the electron-withdrawing effect of the nitro group and therefore DNT shows weak acceptor properties. Buehler and Heaps (*11*) isolated the molecular organic compounds of *m*-dinitrobenzene, DNT, and 2,4-dinitrophenol and determined their melting points. They noted that the least number of molecular compounds are formed with DNT. Sharma and Tiwari (*12*) showed that the charge transfer band with diethylaniline could be used for the spectrophotometric determination of a large number of nitro compounds. However, nitrotoluenes could not be determined by this technique as they show almost no interaction with diethylaniline owing to the presence of the methyl donor group. Herbstein (*13*) has given an interesting discussion of crystalline molecular complexes and he observes that many molecular compounds are unstable at relatively low temperatures and decompose thermally by loss of the components. Foster and Thomson (*14*) isolated the charge transfer complexes *N,N,N′,N′*-tetramethyl-*p*-phenylenediamine with a large number of nitro compounds but they could not isolate satisfactorily the charge transfer complexes of DNT.

The kinetic data for the DNT–DPA reaction at various temperatures and for different particle sizes are best fitted to the equation

$$\xi = k \log t,$$

where ξ is the thickness of the colored boundary, t is the time, and k is a constant. The results are plotted in Fig. 1. The Arrhenius plot gives an experimental energy of 5.5 kcal mole^{-1}.

The rate constant k varies only very slightly with particle size, therefore no useful conclusions can be drawn from this variable.

Nature of the reaction product. In the solid state a charge transfer band is obtained with a maximum at 235 nm (Fig. 2). It is a broad featureless band arising from the no bond to the dative structure of Mulliken (*15*), i.e., the π–π^* transition. The jobs' plot at 235 nm shows that the complex in the solid state is formed in the mole ratio of 1 : 1 (Fig. 3). After the DNT mole fraction of 0.5 the plot falls off smoothly, however, before this it is much less symmetrical which could be due to the presence of a small quantity of a thermolecular species (*16*).

Since the stability of these complexes arises from a shift of the 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 the vibrational spectra may also reveal which part of the molecule plays an active role in complex formation. The ir spectrum of the DNT–DPA molecular complex appears to be a summation of the spectra of the two components, with the vibrational bands of DNT appearing more strongly than those of DPA.

After a systematic study of 40 molecular complexes of picric acid, Kross and Fassel (*17*) noted certain regularities in the ir spectra of the acceptor molecule. According to Kross only the NO_2 asymmetric stretching

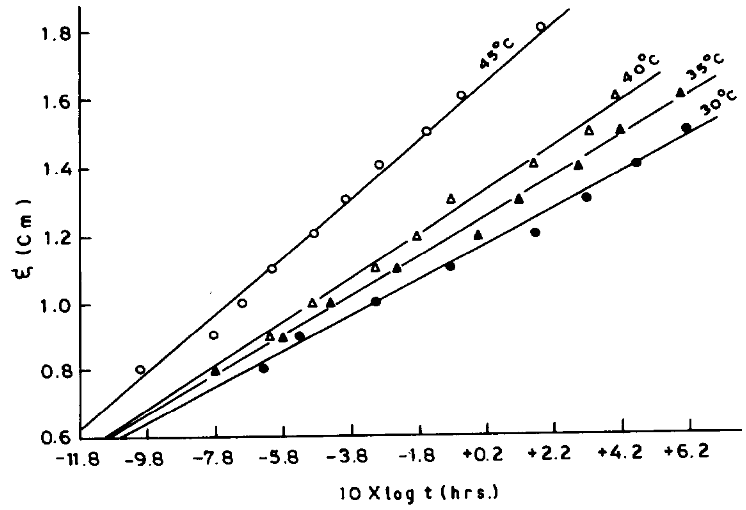

FIG. 1. Kinetic data for the reaction between DNT and DPA at different temperatures in the solid state.

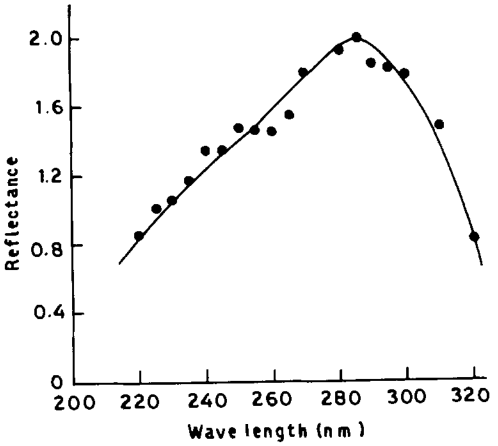

FIG. 2. The charge transfer band of the DNT-DPA complex isolated in the solid state. The reflectance of the reactants was subtracted from that of the complex.

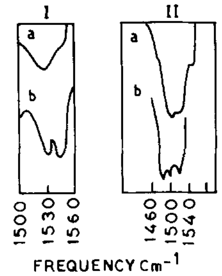

FIG. 4. Nitro asymetric stretching absorption bands. (I). (a) In Picric acid and (b) β-naphthylamine picrate, after Kross and Fassel (Ref. (*17*)). (II). (a) In DNT and (b) the DNT-DPA complex.

vibration and the C-H out-of-plane bending vibration showed significant changes. Assuming that the NO_2 group of DNT behaves like the NO_2 group of picric acid it is possible to interpret the ir spectra of the DNT-DPA complex on the basis of the studies of Kross and Fassel. Just like picric acid DNT shows a broad band with a maximum at 1525 cm^{-1}, due to the two nitro groups present in the molecule. According to Kross and Fassel the donors may be divided into three groups on the basis of their ir spectra. In group 1 there are mostly hydrocarbons which show only one ν_{as} NO_2 band greater in frequency than that in picric acid. The corresponding C-H out-of-plane bending frequencies are all lower than those in picric acid. Such complexes have been classified by Kross as π-π^* complexes. In group 2 he has included about 12 substances where the hydrocarbon donor contains CH_3, OCH_3, OH, and NH_2. In such cases a second band appears at a lower frequency while the first band remains at the original position. These compounds are expected to show, in addition to π-π^* bonding, a localized intermolecular interaction. In group 3 he has included those substances which show a π-π^* and an n-π^* transition. In this case the spectrum shows two ν_{as} NO_2 vibrations, one stronger than the other. The more intense band is located in the region in which the NO_2 vibration is found in picric acid and the weaker band is found at considerably higher frequencies. The C-H out-of-plane vibration invariably occurs at higher frequency than in 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 forms strong localized n-π^* complexes. The charge transfer takes placed between nonbonding orbitals or the

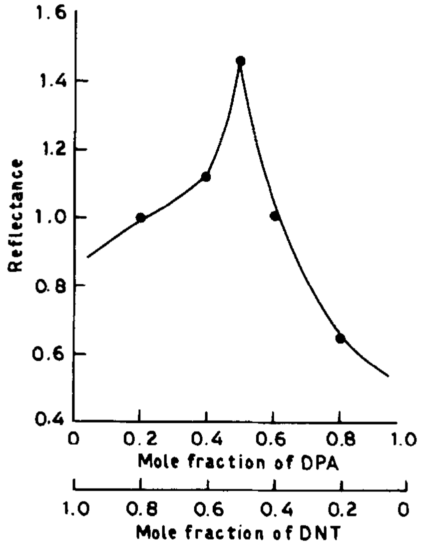

FIG. 3. Job plot for the system DNT-DPA in the solid state by reflectance measurements at 285 nm.

heterocyclic nitrogen atom and the vacant orbital of one of the nitro groups.

A comparison of the spectra given in Fig. 4 shows that we have a π–π^* interaction as well as a localized interaction between the nitro group of DNT and the NH group of DPA. Thus the DNT–DPA complex falls in the second group of the Kross classification. The C–H bands are shifted to lower wavenumbers. The ν_{as} NO_2 splits into two bands denoting differentiation of the energy states of the NO_2 groups in the DA complex. One band is observed at almost the same frequency as the original band of the acceptor while the new band appears at a smaller frequency. Yet another new band appears to give a triplet, which denotes charge transfer as described by Kross.

A further examination of the ir spectra showed that the NH stretching vibration of DPA is shifted by 20 cm^{-1} to a higher frequency in the complex, i.e., from 3400 to 3420 cm^{-1}. This is consistent with a decrease in electron density on the nitrogen atom (*18*). Since the shift in the ν_{as} NO_2 of the order of 10 cm^{-1} it seemed that DPA was more significant as an *n* donor than as a π donor. Since this was in contradiction to most published results it made us suspect that our shift could be due to crystal packing effects (*19*).

TABLE I

CHEMICAL SHIFTS OF VARIOUS PROTONS IN DONOR AND ACCEPTOR MOITIES IN 1.5 *M* DNT + 1.5 *M* DPA IN CCl_4 AT 24°C

Nucleus	Chemical shift in cycles sec^{-1}	Upfield/ downfield
NH proton of DPA	24	Downfield
Aromatic proton of DPA	8	Downfield
a proton of DNT	10	Upfield
b proton of DNT	8	Upfield
c proton of DNT	4	Upfield
CH_3 proton of DNT	4	Upfield

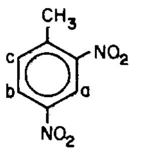

TABLE II

ASSOCIATION CONSTANT (K^{AD}), IN LITER SOLUTION PER MOLE, AND PROTON SHIFTS FOR THE PURE COMPLEX RELATIVE TO THE ACCEPTOR (Δ_0) FOR COMPLEX OF DNT WITH DPA IN CARBON TETRACHLORIDE AT 24°C

Method	Nucleus	K^{AD} (kg mole^{-1})	Δ_0 C/S	λ_{max} (nm)	ϵ_{max}
NMR	H(a)	—	—	—	—
	H(b)	0.35	60	—	—
	H(c)	0.08	100	—	—
	H(methyl)	0.10	133	—	—
Spectroscopic	—	0.23	—	395	1000

To know whether the lone pair on nitrogen of DPA had any significant effect on the complex, some studies were carried out by NMR in CCl_4. The shifts of various protons when a concentrated 1 : 1 mole ratio was used are tabulated in Table I. These results establish that the nonbonding electrons play a much more significant role than do the π electrons. Therefore the ir studies, in conjunction with NMR, establish that in this case DPA is a much more efficient *n* donor than a π donor. Both the ir and NMR results reveal that in DPA the *n* donation is about twice as strong as π donation. The ir studies further reveal that the *n* donation is not to the aromatic ring of the acceptor but instead to one of its nitro groups. This localized interaction is confirmed by the appearance of an additional peak in ν_{as} NO_2 (Fig. 4).

The association constants were determined in solution by NMR and uv–visible spectroscopy and these are tabulated in Table II. This complementary work was done as there is no concept of equilibrium in the solid state, and since all such work has therefore been done in solution, it would make comparisons simpler. If the uv–visible parameter is taken as a standard because it is the average value and compared with similar systems an idea about the extent of bonding may be achieved. The value

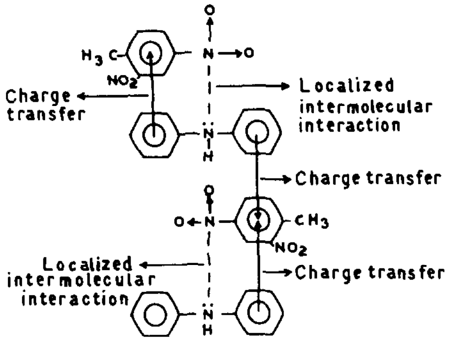

FIG. 5. Proposed structure for the DNT–DPA complex in the solid state.

of the association constant of the aniline–trinitrobenzene CT complex is ten times greater than our system. This is to be expected because DNT is a much weaker acceptor than trinitrobenzene and DPA a much weaker donor than aniline.

It is difficult to postulate the nature of the charge transfer complex in the solid state by means of the chemical evidence presented above. However, according to Foster one obvious fact which emerges is that in the solid state we will have stacks of alternate A and D molecules lying parallel or nearly parallel to one another. However, one is generally considering a species $A_\infty D_\infty$ rather than AD (Fig. 5). The coefficients "a" and "b" measuring the contribution of the no bond and dative structures, respectively, were calculated (*20, 21*) and they were found to be $a^2 \simeq 0.9$ and $b^2 \simeq 0.1$.

In conclusion we can say that in the interaction of DPA and DNT there is a π–π^* CT and an n–π^* localized molecular interaction which is much greater. We reemphasize that these characteristics are applicable to the particular system studied.

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