Clearly, the skeletal distortions correlated above with apparent overlap would show simple relationships with parameters that are either inherently related to the apparent overlap parameter, such as van der Waals radii or Charton's effective steric parameters,⁸ or that were shown to be related to apparent overlap, such as the inversion barriers in 4,5-disubstituted 9,10-dihydrophenanthrenes.³

Experimental Section

Materials. The preparation of the ten compounds used for crystallographic work is described elsewhere.^{3,6}

Crystallographic Data. Crystals were mounted on glass fibers by using cyanoacrylate resin. Data were collected on an Enraf-Nonius CAD4-F diffractometer with Mo K α radiation. Unit cell dimensions were determined by a least-squares fit to the setting angles of 25 independent reflections in the range $15 < 2\theta < 25^{\circ}$. Crystal data are collected in Tables III and IV.

(8) Charton, M. Top. Curr. Chem. 1983, 114, 57. (9) Cosmo, R. Ph.D. Thesis, University of Sydney, 1986.

The structures were solved by direct methods using SHELX-76¹⁰ and refined by full-matrix least-squares methods. All hydrogen atoms were refined with isotropic temperature factors and nonhydrogen atoms were refined anisotropically. Scattering factors used were those provided in SHELX-76. Tables of structure factors, bond lengths and angles, and atom positional and thermal parameters have been deposited as supplementary material.

Calculation of apparent overlap (Σr^*) follows the procedure described earlier¹ and is fully detailed in the suupplementary material.

Supplementary Material Available: Tables of X-ray crystallographic data and ORTEP drawings for a series of 4,5-disubstituted 9,10-dihydrophenanthrenes and 4,5-disubstituted phenanthrenes and procedures for calculation of apparent overlap (Σr^*) (39 pages); tables of observed and calculated structure factors for the 4,5-disubstituted 9,10-dihydrophenanthrenes and 4,5disubstituted phenanthrenes (71 pages). Ordering information is given on any current masthead page.

(10) Sheldrich, G. M. SHELX-76, A Program for X-ray Crystal Structure Determination, University of Cambridge, 1976.

Supercritical Carbon Dioxide.^{1,2} The Cis to Trans Relaxation and π,π^* Transition of 4-(Diethylamino)-4'-nitroazobenzene

Michael E. Sigman and John E. Leffler*

Department of Chemistry, Florida State University, Tallahassee, Florida 32306

Received February 9, 1987

Rates of the cis-trans isomerization of 4-(diethylamino)-4'-nitroazobenzene (DENAB) have been determined for supercritical CO₂ media at 32.4 °C and several densities and DENAB concentrations. A plot of ΔG^* against the Kamlet-Taft π^* solvent parameter has two linear parts, one for the CO₂ media and alkanes and another for more polar solvents. The slope for the CO_2 and alkanes is positive and small, and that for the other solvents is large and negative. It is suggested that the reaction mechanism in the CO₂ media and in alkanes is inversion at one of the azo nitrogens, while in the more polar solvents it is rotation about the bond between the azo nitrogens, for which the transition state is much more polar. The point of intersection of the two lines is at a π^* value of about +0.2. Unlike the ΔG^* values, the E_{\max} of the π,π^* internal charge-transfer band of DENAB are adequately accommodated by a single line.

Introduction

Mechanisms. cis- and trans-azobenzene isomers occupy adjacent energy minima on a multidimensional potential energy surface. The barrier separating the two minima is formed by an avoided crossing of cis and trans surfaces. Since electronically excited states need not be considered, the mechanism of the cis-trans isomerization is known to the extent that it is merely a matter of activating one or more vibrational normal modes.

The transition state will be a region along the top of the barrier that minimizes the free energy of activation. It will be low in energy relative to other parts of the barrier, to minimize the enthalpy of activation, but also broad (i.e., rich in low energy paths) so as to maximize the entropy.

The vibrational modes most likely to be involved are torsion about the N=N bond, angle distortion of one or

both of the N-N-aryl bond angles, and torsion about the N-aryl bond. It should be noted that, since vibrational modes can interact, combined modes are entirely possible and may well offer a more favorable path than any one mode alone.

The choice of vibrational modes has been the subject of controversy. On one side it is claimed that all azobenzene isomerizations proceed by inversion, i.e., distortion of one of the N-N-aryl bond angles.³⁻⁵ This is sometimes called the rehybridization mechanism, since the anglewidening phase of the vibration changes the bond hybridization from sp²-sp² to one more like the sp-sp of a linear N-N-C conformation. Marcandalli et al.⁴ have shown that a plot of $\log k$ for a series of 4-substituted 4'-(diethylamino) azobenzenes in DMF vs. σ^+ and σ^- breaks sharply into two linear parts. The ρ values are -3.15 for the electron-releasing substituents and +10.2 for the electron-withdrawing substituents. Although this would

For previous papers, see: (a) Sigman, M. E.; Lindley, S.; Leffler,
 J. E. J. Am. Chem. Soc. 1985, 107, 1471. (b) Sigman, M. E.; Leffler, J.
 E. J. Phys. Chem. 1986, 90, 6063. (c) Sigman, M. E.; Leffler, J. E. J. Org. Chem. 1987, 52, 1754.

⁽²⁾ Sigman, M. E. "Investigation of Supercritical Carbon Dioxide as a Medium for Organic Reactions" Dissertation, Florida State University, 1986

⁽³⁾ Andersson, J. J. Photochem. 1983, 22, 245

⁽⁴⁾ Marcandalli, B.; Pellicciari-Di Liddo, L.; Di Fede, C.; Bellobono,

I. R. J. Chem. Soc., Perkin Trans. 2 1984, 589.
 (5) Nishimura, N.; Tanaka, T.; Asano, M.; Sueishi, Y. J. Chem. Soc. Perkin Trans. 2 1986, 1839.

Table I. Relaxation Rates in Supercritical CO₂ at 32.4 °C

density ^a g/mL	π^{*b}	10 ⁶ conc, M	$10^2 k, s^{-1}$	
0.95	-0.04	5.98	1.23	
0.95	-0.04	7.61	0.97	
0.93	-0.05	2.1	1.14	
0.92	-0.06	4.73	0.96	
0.92	-0.06	4.56	1.18	
0.75	-0.20	1.6	1.44	
0.75	-0.20	2.83	1.19	
0.75	-0.20	9.46	1.13	
0.75	-0.20	0.98	1.54	
0.75	-0.20	3.97	1.43	
0.70	-0.25	5.98	1.16	
0.65	-0.29	3.26	1.89	
0.59	-0.34	5.33	1.69	
0.59	-0.34	2.24	1.90	
0.59	-0.34	3.65	1.77	
0.59	-0.34	4.99	1.67	
0.59	-0.34	0.97	1 0 9	

^a Interpolated from ref 18. ^b Calculated from a curve through the average values of π^* as a function of density in ref 1a.

ordinarily be interpreted as strong evidence for a change in mechanism,⁶ they interpreted it as support for a single mechanism, inversion.

According to the other side of the controversy,⁷⁻¹⁰ some isomerizations are inversions, but others are rotations involving the N=N torsional vibration. The rotation mechanism is preferred for push-pull¹¹ azobenzenes such as 4-(diethylamino)-4'-nitroazobenzene (DENAB) except when the reaction is conducted in a very nonpolar solvent such as hexane. The cis-trans isomerization rates of the push-pull compounds differ from those of azobenzenes without push-pull substituents in two ways; they are typically faster by orders of magnitude (except in nonpolar solvents), and they are very much more sensitive to changes in the polarity of the solvent. The proposed explanation is that charge-transfer structures such as I, in which the N-N bond is single, lower the force constant of the N==N torsional vibration and become more important as the solvent is made more polar.



A variety of arguments have been used to support claims that two azobenzenes or two series of azobenzenes do or do not isomerize by the same mechanism. These include the magnitude of the change in rate caused by a change in medium or substituent (small in some cases, very large in others), large or small entropies of activation, large or small ΔV^* , comparison with special model compounds, and adherence to or deviation from a particular linear freeenergy relationship.¹²

Supercritical Carbon Dioxide.^{1,2} Supercritical CO₂ is not just one reaction medium but a series of media whose properties as a reaction medium can be varied somewhat without changing the structure of the solvent molecules. The properties that can be adjusted, by changing the



Figure 1. Dependence of k on [DENAB] at the lowest CO_2 density.



Figure 2. Correlation of $\Delta G^*_{305.6}$ with $\pi^* - 0.2\partial$: (•) supercritical CO_2 media; (•) data from ref 10, corrected for the temperature difference.

pressure, include the density, the viscosity, the dielectric constant, and empirical parameters such as π^* . The availability of the CO_2 media extends the range of available low-polarity and low-polarizability solvents a considerable part of the way to the gas phase, until a point is reached at which the desired reagent is no longer sufficiently soluble.

Results

The Cis-Trans Isomerization. The rates of the cistrans isomerization of DENAB at 32.4 $^{\circ}\mathrm{C}$ in CO_2 were measured at DENAB concentrations ranging from $0.9 \times$ 10^{-6} to 9.5×10^{-6} M and at CO₂ densities ranging from 0.59 to 0.95 g mL^{-1} (Table I). These densities correspond to values of the Kamlet–Taft^{1a} π^* ranging from -0.34 to -0.04.

The rate constants in CO_2 range only from 0.97×10^{-2} to 1.98×10^{-2} s⁻¹. For comparison, the rate constants in some conventional solvents, corrected to the same temperature, vary by a factor of almost 10^4 between Me₂SO and benzene.¹⁰

Concentration Dependence. The first order rate constants for the isomerization in CO_2 at a density of 0.59 g mL⁻¹ decrease slightly with increasing total *cis*- plus trans-DENAB concentration, about 15% for a factor of six in concentration (Figure 1 and eq 1a). A similar but

$$k(\text{at } 0.59 \text{ g mL}^{-1}) =$$

2.04 × 10⁻² - (7.10 × 10²)[DENAB] $r = 0.990$ (1a)

rougher correlation can be seen at a CO_2 density of 0.75, but in the 0.92-0.95 density range the variation of k with concentration appears to become random.

$k(\text{at } 0.75 \text{ g mL}^{-1}) =$						
$1.50 \times 10^{-2} - (3.95 \times 10^2)$ [DENAB]	r = 0.76 (1b)					
$k(at \ 0.92-0.95) =$						
$1.20 \times 10^{-2} - (1.98 \times 10^{2})$ [DENAB]	r = 0.32 (1c)					

⁽⁶⁾ Leffler, J. E.; Grunwald, E. Rates and Equilibria of Organic Re-

actions; Wiley: New York and London, 1963. (7) Wildes, P. D.; Pacifici, J. G.; Irick, G., Jr.; Whitten, D. G. J. Am. Chem. Soc. 1971, 93, 2004.

⁽⁸⁾ Asano, T. J. Am. Chem. Soc. 1980, 102, 1205.
(9) Asano, T.; Okada, T.; Shinkai, S.; Shigematsa, K.; Kusano, Y.;
Manabe, O. J. Am. Chem. Soc. 1981, 103, 5161.
(10) Schanze, K. S.; Mattox, T. F.; Whitten, D. G. J. Org. Chem. 1983,

^{48, 2808.} (11) Compounds with an electron-releasing group on one ring and an

electron-withdrawing group on the other

⁽¹²⁾ The same data are often used on both sides of the controversy.



Figure 3. Correlation of DENAB $\pi, \pi^* E_{\text{max}}$ with the Kamlet–Taft solvatochromic π^* parameter: (O) CO₂; (Δ) data from ref 10 for aprotic solvents.

Dependence on π^* . The intercepts of eq 1a-c were used to obtain values of the rate constant at infinite dilution in CO₂ media corresponding to π^* values of -0.34, -0.20, and -0.05. The correlation of ΔG^* with π^* for these CO₂ media, *n*-heptane,¹³ and cyclohexane¹⁴ is shown in Figure 2 (the line at low π^* values) and by eq 2. The

$$\Delta G^*_{305.6} = 20.6 + 1.1\pi^* \text{ kcal} \qquad r = 0.961 \qquad (2)$$

positive slope agrees with the mechanism proposed by Asano,^{8,9} in which inversion occurs at one of the azo nitrogens and the transition state is less polar than the reagent.

Values of $\Delta G^*_{305.6}$ were calculated from the few rates¹⁰ at 25 °C for which activation parameters are available for nonhydroxylic solvents more polar than the alkanes and CO₂. The correlation of these $\Delta G^*_{305.6}$ values with $(\pi^* - 0.2\partial)$ is shown in Figure 2 and eq 3. The 0.2 ∂ correction

$$\Delta G^*_{305.6} = 22.71 - 9.34\pi^* \text{ kcal } r = -0.976 \quad (3)$$

applies only to the aromatic solvents benzene and o-dichlorobenzene, for which ∂ is equal to 1. The value 0.2 for the coefficient has been established by previous medium effect studies.^{4,5}

We believe the change to steep negative slope for the more polar solvents means that the mechanism of the reaction in these solvents has changed to one with a more polar transition state, probably the rotational mechanism.

In solvents of lower polarity, the rotation mechanism is too slow to compete, and the major process is inversion. Apparently the point of equal rates for DENAB is reached at a π^* value of about +0.2.

A similar crossover can be expected when the independent variable is a substituent, with the solvent held constant. The data of Marcandalli et al.⁴ for 4'-substituted 4-(diethylamino)azobenzenes in DMF show a break and change in the slope of the Hammett relationship from -3.15 to +10.2 at a σ value of about +0.2. Where the inversion mechanism prevails, any sp hybridization of the azo N nearest to the 4' substituent would make the charge on the adjacent ring carbon more positive. The energy of this bond dipole would be lowered by electron release from the substituent.

Viscosity. The viscosities of the CO_2 media ranged from less than 0.03 to 1.04 mP. Since the viscosities¹⁵ of the series of CO_2 media are correlated with the density, and hence with π^* , they are necessarily correlated with the relaxation rate constant. However, that correlation is unlikely to have any physical significance.

The π,π^* Absorption of *trans*-DENAB. As expected for a charge-transfer transition, DENAB $E_{\max}(\pi,\pi^*)$ values

Table II					
density, g/mL	π^{*a}	E _{max} , kcal/mol			
1.07	0.06 ^b	63.1			
0.90	-0.08	65.2			
0.86	-0.11	65.4			
0.82	-0.15	65.6			
0.76	-0.20	65.8			
0.73	-0.22	65.9			
0.70	-0.25	66.1			
0.39	-0.34	66.4			
0.34	-0.55°	67.0			

^a Calculated from the best line through the average values of π^* as a function of density in ref 1a. ^b Extrapolated.

decrease with increasing solvent polarity.¹⁰ In contrast to $\Delta G^*_{305.6}$ for the cis-trans isomerization, which required a separate line for the least polar media, both the data from the literature for aprotic solvents and the CO₂ data (Table II) fall close to a single line (eq 4 and Figure 3) when plotted against π^* . This transition is evidently a good model for the transitions in the Kamlet-Taft solvato-chromic indicators.

$$E_{\max}(\pi,\pi^*) = 63.84 - 8.08\pi^* \text{ kcal}$$
 $r = 0.988$ (4)

Experimental Section

DENAB. A solution of 0.69 g of KNO₂ in 10 mL of water was added, with stirring and the temperature maintained below 10 °C, to a cold solution of 1.38 g of *p*-nitroaniline in 50 mL of 20% H₂SO₄. After 5 min, all of the nitrous acid had been consumed (KI starch test), and 1.49 g of *N*,*N*-diethylaniline was added slowly with stirring. After it had been stirred for 1 h at temperatures below 10 °C, the solution was warmed to room temperature and NH₄OH added, giving a dark red precipitate. This was recrystallized three times from acetone-cyclohexane: mp 149-150 °C (lit.¹⁶ mp 151 °C): ¹H NMR & 8.35 (d, J = 9, 2 H), 7.91 (m, 4 H), 6.75 (d, J = 9 Hz, 2 H), 3.5 (q, J = 8 Hz, 4 H), 1.25 (t, J = 8 Hz, 6 H).

DENAB Kinetics. DENAB was dissolved in freshly distilled CH_2Cl_2 , and enough of this solution was transferred to the high-pressure optical cell to give an eventual absorbance of 0.8–1.4. The solvent was then blown off in a stream of dry N_2 and the cell pressurized with CO_2 . The cell was surrounded by a metal block fitted with two 80-W cartridge heaters for temperature control. This assembly was then placed in the sample chamber of a Perkin-Elmer Lambda 5 spectrophotometer. The light from a 500-W slide projector was led to the sapphire cell window by a fiber-optic cable to photoisomerize about 10% of the *trans*-DENAB to the cis isomer.

Thermal relaxation of the *cis*-DENAB was monitored by recording the increase in the optical density of the trans form, by using the time-drive mode of the instrument.

The observed kinetics were first order and at least four orders of magnitude faster than diffusive equilibration with the contents of the dead space in the side arm, valve, and gauge block. Each rate constant in Table I is the average from at least three repetitive excitations and relaxations of a single sample at a given density. The variation within these sets was about 10-15%, but independent determinations at different concentrations showed slightly greater variability, especially at higher CO_2 densities. Each rate constant was determined by a nonlinear least-squares fit of 30 data points at evenly spaced time intervals through a minimum of three half-lives.¹⁷

DENAB $E_{\rm max}$. The cell was loaded and thermostated as described above and the absorption spectrum recorded at a constant temperature. The same sample was used to obtain spectra at lower pressures by slowly venting the cell and recording

⁽¹³⁾ Estimated for 32.4 °C from data in ref 10.

⁽¹⁴⁾ Estimated from the rate constant at 25 °C, correcting to 32.4 °C by means of the activation energy for *n*-heptane.

⁽¹⁵⁾ Stephan, K.; Lucas, K. Viscosity of Dense Fluids; Plenum: New York, 1979.

⁽¹⁶⁾ Beilsteins Handbuch der Organischen Chemie; Springer-Verlag: Berlin; Vol. XVI, p 314.

⁽¹⁷⁾ Moore, P. J. Chem. Soc., Faraday Trans. 1 1972, 1890.

⁽¹⁸⁾ Angus, S., Armstrong, B., deReuck, K. M., Eds. International Thermodynamic Tables of the Fluid State: Carbon Dioxide; Pergamon: New York, 1976; Vol. 3.

the spectrum after the pressure had stabilized. The position of maximum absorbance of the π,π^* band was assigned by taking the median of the two frequencies on either side corresponding to 90% of the maximum absorbance. Each value given in the table is the average of three individual determinations at each density.

The monochromator was calibrated with holmium oxide.

Acknowledgment. We acknowledge support of this work by Grant CHE-8217287 from the National Science Foundation and also the advice of Professor Jack Saltiel.

Effect of Lead Acetate in the Preparation of the Lindlar Catalyst

Judith G. Ulan, Emilio Kuo, and Wilhelm F. Maier*

Department of Chemistry, University of California, Berkeley and the Center for Advanced Materials, Lawrence Berkeley Laboratory, Berkeley, California 94720

Raghaw S. Rai and Gareth Thomas

Department of Materials Science and Mineral Engineering and National Center for Electron Microscopy, Materials and Molecular Research Division, Lawrence Berkeley Laboratory, University of California, Berkeley, California 94720

Received August 5, 1986

The effect of the Lindlar treatment in the preparation of Pd catalysts for the cis-selective hydrogenation of alkynes is investigated with hydrogenation studies on 2-hexyne. The study emphasizes the effect of lead on the hydrogenation selectivity of Pd catalysts. The role of the additives in the catalysts is examined by transmission electron microscopy. The effect of lead deposition on the catalytic activity and selectivity of Pd surfaces is studied with lead-coated Pd foils. No selectivity enhancing effects of the deposition of lead on the Pd particles could be identified.

Cis-selective semihydrogenation of alkynes is receiving on-going attention¹ as an important step in organic synthesis to introduce functionality and stereochemistry simultaneously. A variety of heterogeneous catalysts exist for this transformation, which vary in type of support, added modifiers, and reaction conditions but invariably contain palladium. Despite 35 years of research, the Lindlar²⁻⁴ catalyst, used in uncounted natural product syntheses, still remains the most popular catalyst for this cis-selective semihydrogenation of alkynes.⁵

$$R-C \equiv C-R \frac{H_2}{\text{Lindlar catalyst}} \qquad \begin{array}{c} R \\ C = C \\ H \\ H \end{array}$$

The Lindlar catalyst is a Pd/CaCO₃ catalyst treated with lead acetate solution and used in the presence of 0.05-1molar equiv of quinoline. One well-established action of the quinoline is to inhibit alkene surface interactions, which results in an overall selectivity increase,^{6a} a general concept in selective hydrogenation reactions.^{6b} An undesired side effect is that quinoline also competes with alkynes for Pd surface interaction, which reduces the overall reaction rate.⁷ Quinoline's action as a promoter of morphological changes of the Pd particles, which seems to contribute to the selectivity increase, has been recognized only recently.⁷ A study on the effect of catalyst support on alkyne hydrogenation showed $BaSO_4$ to be superior to $CaCO_3$, the only advantage of the latter was a more effective inhibition of the polymerization side reaction with 1,4-butynediol.⁸ Very little is known about the action of the lead acetate treatment. Our interest in this popular catalyst was stimulated by the expectation of finding and characterizing some form of lead deposition on the palladium particles responsible for the selectivity properties. Such a material could then be synthesized in a controlled fashion and might lead to better catalysts. Doubts about the superior properties of the lead acetate treatment have been raised by Allinger and Cram, who reported improved selectivity obtained with $Pd/BaSO_4$ in the presence of quinoline.⁹ In studies on the partial hydrogenation of 1,4-butynediol Fukuda could only detect reduced catalyst activity with increasing amounts of lead acetate in the Lindlar treatment.¹⁰ It needs to be determined if the lead in fact affects the selectivity of the Pd catalysts at all and if so, what is the exact nature of its effect.

Lindlar had already recognized in his original paper³ that the treatment produces a deposit of metallic lead on the palladium. In a surface science study concerning the effect of lead deposits on Pd (111) single crystals, it was found that lead has little effect on the shape and maxima position of the temperature-programmed desorption spectra of hydrogen but did decrease the amount of chemisorbed hydrogen, indicating only inhibiting effects were operat-

⁽¹⁾ Bartók, M. Stereochemistry of Heterogeneous Catalysis; Wiley and Sons: New York, 1985; Chapter IV. Marvel, E. N.; Li, T. Synthesis 1973. 457

⁽²⁾ Isler, O.; Ronco, A.; Guex, W.; Hindley, N. C.; Huber, W.; Dialer, K.; Kofler, M. Helv. Chim. Acta 1949, 32, 489. Gutmann, H.; Lindlar, H. In Chemistry of Acetylenes; Viehe, H. G., Ed.; M. Dekker; New York, 1969

⁽³⁾ Lindlar, H. Helv. Chim. Acta 1952, 35, 446.
(4) Lindlar, H.; Dubuis, R. Organic Syntheses; Wiley: New York, 1973; Collect. Vol. V, p 880.
(5) Jäger, V.; Viehe, H. G. In Houben-Weyl, Methoden der Organischm Chemie; Müller, E., Ed.; G. Thieme Verlag: Stuttgart, 1977; Vol. War 2007. Va, p 697.

^{(6) (}a) Steenhoek, A.; van Wijngaarden, B. H.; Pabon, H. J. J. Recl. Trav. Chim. Pays-Bas 1971, 90, 961. (b) Bond, G. C.; Wells, P. B. Adv. Catal. 1964, 15, 155.

⁽⁷⁾ Maier, W. F.; Chettle, S. B.; Rai, R. S.; Thomas, G. J. Am. Chem.

⁽a) Fukuda, T. Bull. Chem. Soc. Jpn. 1958, 31, 343.
(b) Cram, D. J.; Allinger, N. L. J. Am. Chem. Soc. 1956, 78, 2518.
(10) Fukuda, T.; Kusama, T. Bull. Chem. Soc. Jpn. 1958, 31, 339.