Table I[a]

| Solvent | Cyclopentenone, *M* | Ratio A:B |
|---|---|---|
| Cyclopentenone neat | 12.4 | 43:57 |
| Benzene | 10.0 | 41:59 |
| | 9.0 | 40:60 |
| | 8.1 | 40:60 |
| | 6.9 | 38:62 |
| | 6.1 | 37:63 |
| | 5.0 | 35:65 |
| | 4.0 | 34:66 |
| | 3.0 | 31:69 |
| | 2.0 | 27:73 |
| | 1.1 | 23:77 |
| | 0.093 | 15:85 |
| 1.0 *M* cyclopentanone in benzene | 1.0 | 27:73 |
| Ethyl acetate | 1.0 | 30:70 |
| *t*-Butyl alcohol | 1.0 | 24:76 |
| 1,4-Dicarbomethoxy-cyclohexane | 2.0 | 35:65 |
| | 1.0 | 33:67 |
| Methanol | 10.5 | 41:59 |
| | 1.0 | 41:59 |
| | 0.1 | 39:61 |

[a] The reactions were run to approximately 10% completion using the light from a Hanovia, 450-w, mercury arc lamp filtered through Pyrex glass. The ratios were determined as noted in footnote *d*, Table II.

Table II[a]

| Solvent | Cyclo-penten-one, *M* | Sensitizer,[b] quencher,[c] or trap (*M*) | Ratio[d] A:B |
|---|---|---|---|
| Benzene | 1.0 | None | 23.3:76.7 |
| | | Xanthone (0.1) | 23.4:76.6 |
| | | Cyclopentene (1.0)[e] | 23.2:76.8 |
| Benzene | 3.0 | None[f] | 31.4:68.6 |
| | | Xanthone (0.1) | 31.5:68.5 |
| | | Xanthone (0.2) | 31.7:68.3 |
| | | Piperylene (0.3) | 31.6:68.4 |
| | | Piperylene (2.1) | 31.4:68.6 |
| Ethyl acetate | 1.0 | None | 29.4:70.6 |
| | | Xanthone (0.1) | 29.6:70.4 |
| Ethyl acetate | 3.0 | None | 35.0:65.0 |
| | | Xanthone (0.1) | 35.1:64.9 |

[a] The reactions were run using 3130-A light to 10% completion. [b] In the order of entry, the xanthone absorbs 91, 76, 87, 92, and 80% of the incident light. [c] The piperylene used contained 26% of the *cis* isomer. Under the conditions of the reaction, little piperylene was consumed. [d] The dimers were separated by vpc on a 5 ft × 3/8 in. column of 10% Carbowax 20M on 45–60 Chromosorb G DMCS at 240°. The ratios were calculated from calibrated integration of the vapor phase chromatograms and are good to ±0.2. [e] The adduct of cyclopentenone to cyclopentene was the major (75%) product. [f] The quantum yield for dimer formation was approximately 0.27.

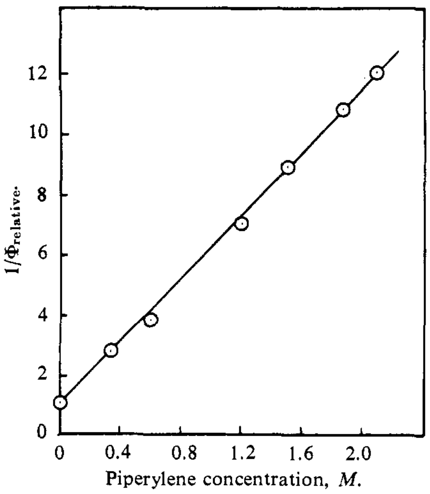

Figure 1. The reactions were run using benzene solutions 3.0 *M* in cyclopentenone and were taken to 11% completion with 3130-A light. The piperylene used contained 26% *cis* isomer. Very little of the piperylene was consumed during the reaction.

The photodimerization of 2-cyclopentenone in the presence of xanthone ($E_{T_1}$ = 74.2 kcal/mole[4]), under conditions where xanthone absorbs most of the incident light, proceeds at nearly the same rate as the dimerization performed in the absence of the sensitizer.[5] This result is in accord with the now classic operational test for the intermediacy of an excited triplet state.[6]

The ratio of the photodimers produced on irradiation of cyclopentenone is a function of the reaction solvent and the concentration of cyclopentenone (Table I). Although on first thought it might appear reasonable to interpret the concentration dependence as an indication that a short-lived, excited singlet state plays a significant role at the higher concentrations, such an interpretation cannot be reconciled with the fact that the dimer ratio (Table II) is independent of the concentration of added sensitizer (xanthone), quencher (piperylene), or trap (cyclopentene). At this time it appears that the concentration effect is no more than a manifestation of a solvent effect; that is, the character of the reaction solvent is strongly dependent on the concentration of cyclopentenone. As is apparent in Table I, the concentration effect can be imitated by alterations in the nature of the solvent. For example, the ratio of the dimers formed on irradiation of 10 *M* cyclopentenone in benzene is very nearly the same as that for irradiation of 1 *M* cyclopentenone in methanol.

It is important to note that the variation in the ratio A:B is really rather small. The extreme values are about 43:57 and 15:85. In our opinion it would be unwarranted to assign special significance to such changes.

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(4) W. G. Herkstroeter, A. A. Lamola, and G. S. Hammond, *J. Am. Chem. Soc.*, **86**, 4537 (1964). We wish to thank Professor Hammond for suggesting in informal conversation the use of xanthone as a sensitizer.

(5) Xanthone, 0.1 *M*, depresses the rate of dimerization of 1 *M* cyclopentenone in benzene by only a factor of 1.16 even though the xanthone absorbs 91% of the incident light. The reduction in rate may be due to either a small amount of quencher present in the xanthone or to a basic inefficiency in the energy-transfer process; *cf.* ref 4.

(6) See, for example, G. S. Hammond, P. A. Leermakers, and N. J. Turro, *J. Am. Chem. Soc.*, **83**, 2396 (1961).

(7) Fellow of the Alfred P. Sloan Foundation.

(8) National Institutes of Health Predoctoral Fellow.

**Philip E. Eaton,[7] William S. Hurt[8]**
*Department of Chemistry, The University of Chicago*
*Chicago, Illinois 60637*

*Received July 20, 1966*

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## Energy Barrier of the *cis–trans* Isomerization of Difluorodiazine

*Sir:*

We wish to report a first attempt at studying the *cis–trans* isomerization of difluorodiazine and deter-

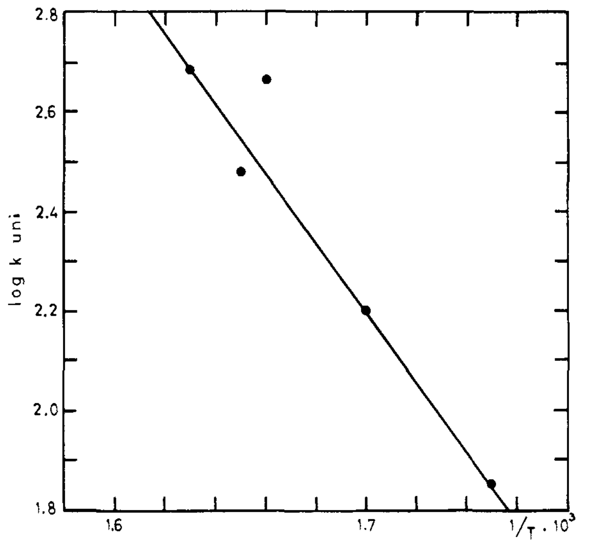

Figure 1. A plot of log $k_{\mathrm{uni}}$ *vs.* $1/T$ for the *cis–trans* isomerization of difluorodiazine.

mining the isomerization barrier under homogeneous conditions.

Difluorodiazine ($N_2F_2$) is known to exist in two isomeric forms which differ in their chemical reactivity.[1] The structure of the chemically less active isomer is very well established,[1-3] having a *trans* configuration. Two different structures have been proposed for the chemically active isomer:[3-5] a *cis* structure and a 1,1-difluorodiazine, $F_2N{=}N$. There is, however, quite clear evidence that the active isomer has a *cis* configuration.[4-6] Recently the heats of formation of the two isomers have been measured, the *cis* isomer being more stable by 3 kcal/mole.[7]

While there have been a few attempts at studying the isomerization process,[1,8] none could be carried out under homogeneous conditions. In all the reported studies, the isomerization was catalyzed by the heated metal reaction vessels. Difluorodiazine attacks glass at elevated temperatures. This phenomenon itself prevents any attempt at studying the isomerization reaction under homogeneous conditions in a hot glass vessel.

In this study, *trans*-difluorodiazine, highly diluted in argon (~1:70), was heated in a single-pulse shock tube. In this technique the reaction mixture is heated by reflected shock waves to elevated temperatures where it is maintained and reacts for a short period of time (~2 msec) and is then rapidly cooled by an expansion wave.[9] Reaction dwell times could be read from the recorded oscilloscope traces to within ±10%. The tube walls remain cold in this gas-dynamic procedure; heterogeneous wall catalysis is thus eliminated, and the reaction can be studied under purely homogeneous conditions.

The difluorodiazine used in this study was prepared by fluorination of sodium azide with elementary fluorine according to Pankratov, *et al.*[10] The reaction product consisted of a mixture of the two isomers. The *cis* isomer was quantitatively removed by a reaction with $AsF_5$[11] to yield a solid complex $N_2F^+AsF_6^-$. The remaining material contained a few per cent of $NF_3$ and $N_2O$, but no *cis*-$N_2F_2$. All analyses were carried out by vpc using a 3-m silica gel column. The inlet system as well as the thermal conductivity cell and filaments were made of nickel.

The isomerization was studied over the temperature range 570–615°K and pressures up to 1.6 atm. One additional peak appeared in the shock-heated sample. Its retention time by vpc was exactly the same as for the *cis* isomer. For additional identification, the shocked gas of one particular run was divided into two portions. One portion was analyzed by vpc directly, while the second one was exposed to $AsF_5$ for several minutes prior to its analysis. The additional peak which showed up in the first portion disappeared completely in the second one. This suggests that the reaction product is indeed the *cis* isomer. Mass balance of difluorodiazine at the above-mentioned temperature range was maintained to within 10%. At higher temperatures the difluorodiazine begins to decompose, probably to elementary nitrogen and fluorine.

First-order rate constants were computed from the ratio of the *cis* to the *trans* peak areas. The equilibrium constant of the reaction (about 20 at the above-mentioned temperature range) was computed from the heat of isomerization,[7] together with $\Delta C_p°$ and $\Delta S°$, which were obtained from the assigned six vibrational frequencies of the two isomers.[4]

A plot of log $k_{\mathrm{uni}}$ *vs.* $1/T$ is given in Figure 1. From the figure we get

$$k_{\mathrm{uni}} = 10^{14} \exp(-32200/RT)\ \mathrm{sec}^{-1}$$

The preexponential factor obtained is rather high and similar to its analog in the carbon–carbon double-bond system.[9,12] It is obvious that the transition state in the *cis–trans* isomerization of difluorodiazine does not involve a triplet excited state. There is, however, a marked difference in the barrier for the isomerization in the N=N and C=C systems. The activation energy for rotation about a carbon–carbon double bond ranges from 56 to 65 kcal,[9,13] depending on the particular substituents involved. The transition state is compatible with one in which the $\pi$-bond overlap is decoupled by rotation. This always requires the rupture of one of the C=C bonds.

The energy requirement of this process can be fairly well estimated from the difference in the heat of reaction of the following two steps. This difference is ~60 kcal/mole, a value very similar to the experimental activation energy of the isomerization process. The assumption that the isomerization proceeds *via* rotation about the C=C bond is very reasonable.

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(1) C. B. Colburn, *et al.*, *J. Am. Chem. Soc.*, **81**, 6397 (1959).

(2) S. H. Bauer, *ibid.*, **69**, 3104 (1947).

(3) R. H. Sanborn, *J. Chem. Phys.*, **33**, 1855 (1960).

(4) R. Ettinger, *et al.*, *ibid.*, **34**, 2187 (1961).

(5) J. F. Herron and V. H. Dibler, *J. Res. Natl. Bur. Std.*, **65A**, 405 (1961).

(6) R. K. Bohn and S. H. Bauer, *Inorg. Chem.*, **5**, in press.

(7) G. T. Armstrong and S. Marantz, *J. Chem. Phys.*, **38**, 169 (1962).

(8) M. Lustig, *Inorg. Chem.*, **4**, 104 (1965).

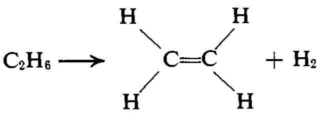
(9) A. Lifshitz, S. H. Bauer, and E. L. Resler, Jr., *J. Chem. Phys.*, **38**, 2056 (1963).

(10) A. V. Pankratov, *et al.*, *Zh. Neorg. Khim.*, **9**, 2030 (1964); *Chem. Abstr.*, **61**, 10299*f* (1964).

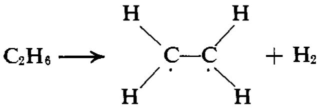
(11) D. Moy and A. R. Young, II, *J. Am. Chem. Soc.*, **87**, 1889 (1965).

(12) J. E. Douglas, B. S. Rabinovitch, and F. S. Looney, *J. Chem. Phys.*, **23**, 315 (1955).

(13) E. W. Schlag and E. Kaiser, Jr., *J. Am. Chem. Soc.*, **87**, 1171 (1965).

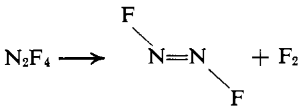


$\Delta H = \Delta H_f(C_2H_4) - \Delta H_f(C_2H_6) = 33$ kcal



$\Delta H = 2D(C_2H_5\text{-}H) - D(H\text{-}H) = 93$ kcal

In nitrogen the energy required to decouple the $\pi$-bond overlap is even higher. Computation similar to the above yields approximately 84 kcal.[7,14]



$\Delta H = \Delta H_f(t\text{-}N_2F_2) - \Delta H_f(N_2F_4) = 19.6$ kcal

$N_2F_4 \longrightarrow F\text{-}\underset{\cdot}{N}\text{-}\underset{\cdot}{N}\text{-}F + F_2$

$\Delta H = 2D(N_2F_3\text{-}F) - D(F\text{-}F) = \sim 104$ kcal

The experimental 32-kcal activation energy for the isomerization of difluorodiazine is far too low when compared to the rotational barrier of 84 kcal. The nitrogen–nitrogen bond in the transition state has essentially a double-bond character.

The only transition state which might lead to isomerization from the ground state is that having a *linear configuration*, which may not require the high energy needed to overcome a rotational barrier. A transition state of this kind is impossible in the >C=C< system.

**Acknowledgment.** The authors wish to thank Professor S. H. Bauer of Cornell University for very valuable correspondence on this matter.

(14) A. V. Pankratov, *Russ. Chem. Rev.*, 32, 157 (1963).

(15) In partial fulfillment of the requirements for a Ph.D. thesis to be submitted to the Senate of the Hebrew University by J. B.

**J. Binenboym,[15] A. Burcat, A. Lifshitz, J. Shamir**
*Department of Inorganic Chemistry*
*The Hebrew University, Jerusalem, Israel*

*Received August 2, 1966*

## Photoinduced Substitution. IV. Reaction of Aromatic Nitro Compounds with Hydrochloric Acid[1,2]

*Sir:*

Aromatic nitro compounds are found to react in a relatively clean fashion with concentrated hydrochloric acid when irradiated with ultraviolet light >290 mμ. The major reaction in each case involves reduction of the nitro group to an amino group and replacement of three aromatic hydrogen atoms by chlorine.

The light source used in these studies was a 1200-w G.E. photochemical lamp;[3] radiation below 290 mμ was excluded by a Pyrex filter. Each photoproduct reported was characterized by a mixture melting point with an authentic sample and by the coincidence of the infrared spectrum with that of the known compound.

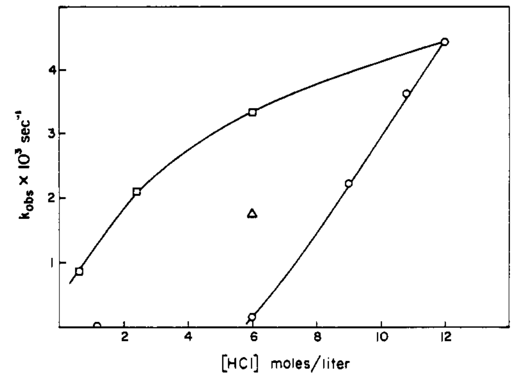
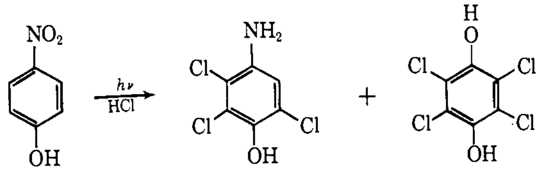
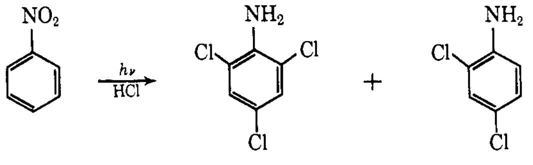


Figure 1. Photoreaction of nitrobenzene in hydrochloric acid: —○—, no added salt; —□—, sufficient LiCl added to give a total chloride concentration of 12 *M;* —△—, 3 *M* LiCl present.

When a 2.5 × $10^{-4}$ *M* solution of *p*-nitrophenol in concentrated hydrochloric acid was irradiated for 1 hr at room temperature in a cuvette, $\lambda_{max}$ shifted from 320 mμ (*A* 2.02) to 290 mμ (*A* 0.74); very little change occurred on further irradiation. For characterization of the products, a solution of 348 mg of *p*-nitrophenol in 250 ml of concentrated hydrochloric acid in a 500-ml Pyrex flask was flushed with nitrogen and irradiated for 93 hr, at which time the reaction was complete as indicated by the spectrum of a diluted aliquot. Neutralization of the acid, extraction with benzene, and chromatography of a portion (83%) of the extracted products on silica gel yielded 315 mg (71%) of 2,3,6-trichloro-4-aminophenol, mp 170.5–171°, and 84 mg (16%) of tetrachlorohydroquinone, mp 230–232°. Similarly, *m*-nitrophenol gave 2,4,6-trichloro-3-aminophenol (37%) and 4,6-dichloro-3-aminophenol (24%) as the principal products.



Nitrobenzene reacted somewhat faster than the nitrophenols; the reaction was essentially complete ($\lambda_{max}$ 273 mμ (*A* 1.38) → $\lambda_{max}$ 288 mμ (*A* 0.28)) within 25 min when a 2 × $10^{-4}$ *M* solution of nitrobenzene in concentrated hydrochloric acid was irradiated in a cuvette. In preparative experiments 2,4,6-trichloroaniline (44–62% yields) and 2,4-dichloroaniline (~10%) were obtained from mixtures of nitrobenzene (308 mg) in 500 ml of concentrated hydrochloric acid irradiated for 10 hr.



Rate data for the decrease in absorbance at 273 mμ for solutions of nitrobenzene (1 × $10^{-4}$ *M*) in hydrochloric acid of varying concentrations are presented in Figure 1. The reactions were carried out at 25° in cuvettes with a 1-cm light path. Though the over-all reaction is undoubtedly complex, the decrease in absorbance fol-

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(1) Part III: R. L. Letsinger and J. H. McCain, *J. Am. Chem. Soc.*, 88, 2884 (1966).

(2) This work was supported by a Public Health Service Fellowship (1-Fl-GM-29, 771-01 awarded to G. G. W.) and by a National Science Foundation Grant (GP-5715).

(3) R. L. Letsinger, O. B. Ramsay, and J. H. McCain, *J. Am. Chem. Soc.*, 87, 2945 (1965).