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SOLVENT EFFECT ON THE PHOTODIMERIZATION OF ACENAPHTHYLENE

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An intriguing report that the photodimerization of acenaphthylene in benzene produces the trans cyclobutane isomer while the same dimerization performed in cyclohexane produces the cis isomer has persisted in the photochemical literature from 1913 to the present time (1,2). We wish to present here some of our preliminary findings on the solvent effect on the photodimerization of acenaphthylene.

Acenaphthylene in various solvents (see Table I) was irradiated in a flask designed to fit around a Hanovia quartz immersion well. Unless otherwise specified the solutions were stirred magnetically and continuously purged with purified nitrogen. A Hanovia 450-w medium-pressure mercury arc lamp inside a uranium glass filter sleeve was used in all experiments. The use of the filter sleeve (cut off at 3300Å) allowed the excitation of the acenaphthylene at the mercury lines (3650, 4045, 4358Å) while preventing the excitation of cis and trans products at the 3130Å mercury line. Analyses of the reaction mixtures were accomplished by u.v. spectrophotometric analysis and by isolation of all components by column chromatography. The results are summarized in Table I.

First, it is interesting to note that at the concentrations studied both cyclohexane and benzene give a preponderance of the cis isomer. Consequently, it must be concluded that the trans isomer predominated in earlier studies either because of a relatively poor material balance or because of photoisomerization and photodecomposition of the initially formed product. There is a gradual reduction in the cis-trans ratio as one proceeds from methanol to cyclohexane to benzene (5.7, 4.2, 2.4). This is the trend one might expect if molecular complexes were important in the formation of the cis isomer. This trend roughly parallels solubility of acenaphthalene in these solvents. However, no indication of a ground state complex could be found by spectrophotometric studies. Tris (acetylacetanato) Iron (III)

TABLE I

Solvent Effect on the Photodimerization of Acenaphthylene[1]

SOLVENT	[illegible]	Products			$\frac{Cis}{Trans}$	% Reaction	% Cis	% Trans	% Material Balance
		Trans (g)	Cis (g)	Ac(g)[3]					
1. Cyclohexane	-----	1.26	5.25	8.40	4.17	42.8	80.6	19.4	98
2. Cyclohexane	1×10^{-4} M $Fe(AA)_3$[4]	1.47	5.01	7.77	3.41	42.7	77.3	22.7	94
3. Benzene	-----	2.82	6.80	5.27	2.41	63.2	70.6	29.4	98
4. Benzene	1×10^{-4} M $Fe(AA)_3$	2.52	6.42	5.97	2.55	58.8	71.8	28.2	99
5. Benzene	O_2 flush[5]	0.11	5.84	9.18	53.	39.1	98.2	1.85	99
6. Methanol	-----	0.93	5.34	8.71	5.74	41.3	85.2	14.8	98
7. n-Propyl Bromide	-----	10.01	4.06	0.84	0.41	92.6	28.8	71.2	98

1. In all reactions reported 150 ml of solvent and 15.2 grams of acenaphthylene were used. Photolysis time in each case was 15.0 hours and the temperature of the solution was maintained at 25°.

2. Products were determined by isolation and by spectrophotometric methods. Synthetic mixtures indicated that the analytical methods were accurate to less than 1%. Accuracy was somewhat lower in the cases where $Fe(AA)_3$ was used.

3. Acenaphthylene recovered.

4. Tris (acetylacetanato) Iron (III).

5. The solution was continuously purged with oxygen.

showed little quenching effect on the dimerization in cyclohexane or benzene. The reduction in the percent reaction is due to a small filter effect since the chelate absorbs about 5% of the 3650Å light at a concentration or 10^{-4}M. Oxygen slightly reduces the amount of the *cis* isomer formed but almost completely eliminates the formation of the *trans* isomer (29% to 2%).

This can be rationalized by two mechanisms:

Mechanism A

1. $A + h_{\nu} \rightarrow A^{s}$
2. $A^{s} \rightarrow A$
3. $A^{s} \rightarrow A^{t}$
4. $A^{t} + A \rightarrow A_2^{t} \rightarrow A_2$ (predominantly *trans*)
5. (A...A) molecular complex + $h_{\nu} \rightarrow (A...A)^{s}$
6. $(A...A)^{s} \rightarrow (A...A)^{t}$
7. $(A...A)^{s,t} \rightarrow A_2$ (predominantly *cis*)
8. $A^{t} + O_2 \rightarrow A$

Mechanism B

1. $A + h_{\nu} \rightarrow A^{s}$
2. $A^{s} \rightarrow A$
3. $A^{s} + A \rightarrow A_2$ (predominantly *cis*)
4. $A^{s} \rightarrow A^{t}$
5. $A^{t} \rightarrow A$
6. $A^{t} + A \rightarrow A_2^{t} \rightarrow A_2$ (predominantly *trans*)
7. $A^{t} + O_2 \rightarrow A$

Mechanism A, a modification of Bowen's mechanism (3) is consistent because of the molecular complex with the (methanol, cyclohexane, benzene) solvent effect observed and the reduction of the *trans* isomer formed on triplet quenching (reaction A-8). It seems reasonable that the π-complex would produce the *cis* isomer (reaction A-7) because of required π-complex geometry. It is also reasonable that this π-complex singlet or triplet eximer would be shorter lived (4) and consequently harder to quench with oxygen than the acenaphthylene triplet. It is not possible with our present data to distinguish between the singlet or triplet eximers.

Mechanism B can nicely account for the oxygen quenching result but cannot easily account for the (methanol, cyclohexane, benzene) solvent effect unless the quantum yield for intersystem crossing is solvent dependent (reaction B-4). At the present time there is little experimental evidence on this point.

When n-propyl bromide is used as a solvent the amount of cis isomer formed is slightly reduced (4.06 vs. 5.34, 6.80, 5.25) but the extent of conversion and the amount of the trans isomer formed are drastically increased (10.01 vs. 0.93, 3.83, 1.26). This is consistent with mechanism A where the equilibrium concentration of the π-complex is not appreciably changed (consequently the amount of the cis isomer formed is only slightly changed) and where this solvent facilitates intersystem crossing (reaction A-3) via the heavy atom effect (5).

This is apparently the first example reported of a photochemical reaction being strongly influenced by a heavy atom solvent(6). Mechanism B can explain the increase in cis product in the n-propyl bromide solvent (reactions B-4 and 6) but would predict a concurrent reduction in the product formed from the singlet reaction (reaction B-3) because of the increased crossing to the triplet state (reaction B-4).

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