

Some Notes on Charge Transfer Interaction between Iodine and Polynuclear Aromatic Hydrocarbons

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based upon a value of about $0.2 \pi a_0^2$ (a_0 = radius first Bohr orbit of H atom) for the collision cross section for the $^3\Sigma_u^+$ and $^3\Sigma_g^+$ excitations. The experimental evidence obtained by Poole for the dc discharge, the data of Corrigan and von Engel for a 5-Mc/sec discharge, and the present data for a 3000-Mc/sec discharge are in good agreement and suggest that the collision cross section is about 2 to 3 times as large as the theoretical value.

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¹ J. P. Wittke and R. H. Dicke, *Phys. Rev.* **103**, 620 (1956).

² H. G. Poole, *Proc. Roy. Soc. (London)* **A163**, 424 (1937).

³ S. J. B. Corrigan and A. von Engel, *Proc. Roy. Soc. (London)* **A245**, 335 (1958).

⁴ Lunt, Meek, and Smith, *Proc. Roy. Soc. (London)* **A158**, 729 (1937).

On the Identity of the Green Forms of Bianthrone

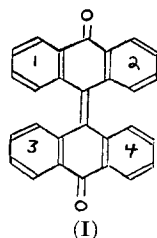
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YELLOW dehydrobianthrone (I) can be transformed into a metastable green material by heat, pressure, and low-temperature irradiation.¹ Hirshberg and Fischer conclude from the similarities of the absorption bands in the visible that the thermochromic and photochromic forms are identical.² On the other hand, Kortum, Theilacker, and their co-workers conclude that the thermochromic and



piezochromic forms are identical and differ from the photochromic form in both spin multiplicity and nuclear configuration.¹ They suggest that the thermo-

TABLE I. First-order rate constants for the disappearance of the green forms of bianthrone.*

$T^\circ\text{C}$	Thermo	Piezo	Photo
-41	156	163	175
-77	1.10	1.02	1.07

* In units of 10^{-3} sec^{-1} . Solvent: 50% EtOAc-50% $\text{C}_2\text{Cl}_4\text{H}_2$ vol.

chromic species is a singlet in which rings 1 and 4 are above the plane of the paper while rings 2 and 3 are below it. Each of the "anthrone" halves of the molecule is approximately planar and they are twisted about the double bond which remains intact. The photochromic form is postulated to be a biradical in which the two halves are perpendicular to one another. Both forms transform into the yellow species in which rings 1 and 2 are above the plane of the paper and rings 3 and 4 below, as determined by x-ray diffraction.³

This explanation implies that the photochromic form is more stable than the thermochromic. The former has less steric strain which requires a higher activation energy. It must also undergo a nonadiabatic transition to become singlet (I) yielding a lower frequency factor.

We have determined the kinetics of the transformation of the green to the yellow form in solution at -77° and -41° . The thermochromic form was prepared by subliming (I) at 10^{-3} mm onto a surface cooled by liquid nitrogen. The piezochromic form was obtained by grinding (I) in a mortar. Solutions of both solids were prepared in the absence of light at -77° . The photochromic form was prepared by irradiation of the solution of (I) at $\sim -100^\circ$. The rate of transformation from green to yellow was followed by noting the disappearance of the absorption at $650 \text{ m}\mu$, near the absorption maximum of the green form. The rates were strictly first order. See Table I.

Within the 10% uncertainties, the rates are identical for similar conditions. Since the absorption band followed is the one responsible for the green color of the metastable forms, we conclude that the three forms are identical.

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¹ G. Kortum, *Angew. Chem.* **70**, 14 (1958), and references cited therein.

² Y. Hirshberg and E. Fischer, *J. Chem. Soc.* **1953**, 629.

³ E. Harnik and G. M. J. Schmidt, *J. Chem. Soc.* **1954**, 3295.

Some Notes on Charge Transfer Interaction between Iodine and Polynuclear Aromatic Hydrocarbons

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IN a previous communication it was shown by Bhattacharya and Basu¹ that the stabilization energy for the charge transfer complexes between iodine and a number of polynuclear hydrocarbons was constant and was greater than the electrostatic energy between ion pairs separated by a distance of 3-4 Å.

TABLE I. Charge transfer interaction energies in I₂-polynuclear hydrocarbon systems.^a

Compound	Carbon tetrachloride ($\epsilon=2.24$)		Chloroform ($\epsilon=4.90$)		<i>n</i> -Heptane ($\epsilon=1.97$)		<i>I.P.</i> (ev)
	λ ($m\mu$)	$h\nu$ (ev)	λ ($m\mu$)	$h\nu$ (ev)	λ ($m\mu$)	$h\nu$ (ev)	
Naphthalene	360	3.45	357	3.48	255	3.50	8.30
Anthracene	430	2.89	422	2.94	418	2.97	7.74
Pyrene	420	2.96	412	3.02	410	3.03	7.82
Chrysene	394	3.15	387	3.21	375	3.31	8.04
Phenanthrene	378	3.29	378	3.29	373	3.33	8.27
Biphenyl	340	3.65	334	3.73	333	3.72	8.55
Stilbene	373	3.33	364	3.41	360	3.45	7.99

^a Concentration of hydrocarbon was less than 0.1M and that of iodine was one-hundred times less.

It was suggested that there was appreciable covalent contribution in the stabilization of these complexes. It may further be suggested that if the electrostatic contribution be the primary cause for the stabilization of these complexes then the energy necessary to bring about charge transfer should depend on the dielectric constant of the medium. In Table I are given the charge transfer interaction energy for the I₂-polynuclear hydrocarbon systems in three different solvents. It is evident that the charge transfer energy is not appreciably affected by the change in the dielectric constant of the medium. The $h\nu$ vs *I.P.* plot was linear in all the three solvents with a slope close to unity and a constant intercept, which means a constant stabilization energy. It may therefore be concluded that the charge transfer is intramolecular rather than intermolecular, i.e., the charge transfer is taking place between molecules held together by forces other than electrostatic.

Thanks are due Dr. S. Basu for his helpful guidance and the Council of Scientific and Industrial Research, India, for a Junior Research Fellowship.

¹ R. Bhattacharya and S. Basu, *Trans. Faraday Soc.* **54**, 1286 (1958).

Separation of the Hydrogen Isotopes by Preferential Adsorption at 20.4°K*

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IT was first demonstrated by Taylor *et al.*¹ and later in a more comprehensive investigation by Edse and Harteck² that the hydrogen isotopes could be separated by desorption from suitable surfaces at low temperatures. The separation factors, for small surface coverages, reported by Harteck *et al.*^{2,3} were quite large. Due to the slow desorption (many days) required for the isotope separation and the temperature

dependence of the separation factor, it was suggested³ that the separation was controlled principally by a "tunnel effect" in the diffusion of the gas through the adsorbent. From the recent experiments of Cunningham, Chapin, and Johnston,⁴ where large *ortho-para* separation factors due to preferential adsorption were observed under conditions of appreciable surface coverages, pressures and mass flows, it would seem that the above kinetic mechanism is not generally applicable. The purpose of this note is to show that under conditions similar to those in the *ortho-para* experiments, large isotope separations can be obtained, and that the magnitude of the separation factors can be accounted for, purely from thermodynamic considerations when only quantum zero point effects are considered.[†]

The apparatus was a modified version of the single stage *ortho-para* separator⁴ containing γ -alumina, and the experimental procedure was the same. The compositions of the desorbed gas at various times for two different experiments, are given below. The time is not directly proportional to the amount desorbed, since the pumping rate varied. Only from $\frac{1}{3}$ to $\frac{1}{2}$ of the material was desorbed from the alumina when the last sample was taken.

The composition (mole %) of the feed gas in experiment I was 49.6% normal deuterium, 50.4% normal hydrogen. The composition of the last effluent gas was 37.6% deuterium. Insufficient material had been passed through the separator to achieve a steady state. In experiment II the feed gas was 62.0% normal deuterium 38% *para* hydrogen.[‡] The last effluent gas contained 58.6% deuterium. (See Table I.) If sampling had continued, 100% deuterium would have been obtained after approximately 12 minutes. The separation factor is so large (probably in excess of 30), than it cannot be determined from experiments containing any appreciable amount of deuterium in the feed gas.

The experimental results can be accounted for on the basis of a simplified model for the adsorbed phase. Consider the adsorbed phase as a mobile monolayer, in which the electronic states and internal vibrations