

Caging Effect in the Photolysis of Ethyl Iodide

By Jae Ho Choi* and John E. Willard**

요오드화에틸의 光分解에 있어서의 Cage 効果

崔 載 鎬 · John E. Willard

(1962. 6. 26 受理)

I. Introduction

When a C_2H_5I molecule in a hydrocarbon solvent absorbs a quantum of 2537 Å light, it always dissociates. If, however, it is surrounded by a cage of solvent molecules, the radical and atom may lose their energies to the cage walls and immediately recombine, or they may recombine by diffusion after having escaped only a molecular diameter or so from each other. I_2 , as a scavenger, reacts with radicals and thus an exchange reaction occurs. The purpose of this work has been to measure the relative effectiveness of several hydrocarbons as solvents in preventing the escape of C_2H_5 radicals from a solvent cage using the fact⁽¹⁾ that the quantum efficiency for exchange of the molecules which absorbs quanta for which the C_2H_5 radical and I atom formed escape recombination either in the parent cage or by diffusive recombination.

II. Experimental Part

Purification of Materials. Eastman white label ethyl iodide was purified by passing it through a 35 cm. column filled with Alcoa F-20 activated alumina. It was then distilled on a Todd column packed with glass helices and the center cut was obtained. The distillate was again passed through alumina and stored in a brown bottle in the desk.

Phillips pure grade n-pentane, isopentane and cyclopentane were mechanically stirred with successive

portions of concentrated H_2SO_4 until further portions showed no coloration. They were then extracted with water, dried over $MgSO_4$ and fractionally distilled on a Todd column.

I^{131} was obtained in carrier-free NaI^{131} solution containing sulfite and a trace (0.005%) of benzyl alcohol. The specific activity was usually of 1 millicurie/ml.

The following materials were used without purification: NaI , Baker U. S. P., CCl_4 , Analytical reagent, and Na_2SO_3 , Mallinckrodt Analytical grade.

Photolysis Equipment. The illumination for all photolysis in the cryostat was provided by two Hanovia SQ 2537 110 ma. low pressure mercury lamps with thin quartz windows. Corning 791 (Vycor) filters were used to exclude light of wave length shorter than 2400 Å. The entire lamp, excluding windows, was wrapped with asbestos. A few turns of nichrome heater wire were wrapped around the edge of the window of each lamp to prevent condensation of mercury vapor on the window. The cryostat consisted of a square copper block mounted vertically to accept a 1 cm square quartz allow for a light path through the block and cell. The copper block serves to maintain an even temperature distribution around the cell.

Preparation of Samples. The reaction cells were made from rectangular quartz stock of 1.2 cm \times 1.2 cm and 1 mm. wall thickness. Each cell was fastened by means of a graded seal to a pyrex 8 mm. I.D. tube, containing a glass bulb blown from 6 mm. I.D. pyrex tubing at the opposite end. The entire reaction vessel, cell, tube, and bulb, altogether

* Atomic Energy Research Institute, Korea.

** Department of Chemistry, University of Wisconsin, Madison, Wisconsin, U.S.A.

25-30 cm. long, was connected at the middle to the vacuum line by means of ST joint.

3 ml. of a hydrocarbon solution containing 1 mole % of C_2H_5I was pipetted into a pyrex thimble. This was then frozen down in liquid air, and sealed by means of ground joint onto the vacuum line. Degassing was repeated four times followed by distillation into the reaction cells through P_2O_5 . After the C_2H_5I in hydrocarbon solution had been distilled over, the I_2 was introduced by the method described below.

A 0.012 *M.* NaI solution was prepared. A 0.5 ml. of this solution was micropipetted into a small test tube made from 8 mm. I.D. pyrex tubing. A small amount of (2-5 microcuries) NaI^{131} was added to this test tube. The solution was then evaporated down to crystals of NaI by circulating clean dry air over the surface of the liquid as it was gently heated in a water bath. The test tube was then placed in the drying oven (110°C) for 2 minutes to insure complete crystallization. The NaI crystals were then covered with an excess of reagent grade $K_2Cr_2O_7$ and the test tube was sealed onto the vacuum line. The NaI- $K_2Cr_2O_7$ was fused in vacuo by applying a small flame to the outside of the tube. The I_2 produced by oxidation of I^- was distilled through P_2O_5 into the quartz cell. The fusing operation was repeated three times with 20 minutes intervals between each heating. After 30 minutes the cell was sealed off from the vacuum line. This procedure, designed to produce an iodine concentration of 10^{-3} *M.* in a 3 ml. sample resulted in a 70% to 80% transference of I_2 to the cell, giving an initial iodine concentration of $2-8 \times 10^{-4}$ *M.*

Spectrophotometric Equipment. To measure initial iodine concentration a Beckman D.U. spectrophotometer was used. The determination of the iodine concentration in hydrocarbon solution was made at 5200 Å where the extinction coefficient is 900. The iodine concentration in C_2H_5I was determined at 4780 Å with $E=1280$.

Extraction of Sample. After photolysis, the solution in the cell was allowed to flow into the glass bulb mounted on the end of the reaction cell. The bulb containing sample was frozen down in

liquid air, and sealed off from the reaction tube. The bulb was placed in wide necked separatory funnel and broken under a mixture of 22 ml. of aqueous Na_2SO_3 and 25 ml. of CCl_4 . The CCl_4 layer was drained off into a smaller separatory funnel after 2 minutes vigorous shaking, and the SO_3 solution remained was washed with 5 ml. of fresh CCl_4 and this was separated, and the total volume of CCl_4 layer was washed with fresh SO_3 solution. After the final separation, the two total volumes were drained into 50 ml. aliquot of inorganic phase, diluted with 4 ml. of fresh SO_3 solution, were counted on a well type scintillation counter described in detail by Hanrahn.⁽²⁾

The equipment included: an Atomic Instrument Co. Model 810 well type scintillation detector, with a thallium activated sodium iodide crystal, a DuMont photomultiplier tube with a linear preamplifier, and an Atomic Instrument Co. linear amplifier Model 218 used with an Atomic Scaler Model 1030 A. The high voltage supply was an Atomic "super stable" Model 312.

III. Results

Spectrophotometric Determination of Rates of Iodine Production. When pure ethyl iodide was photolyzed at room temperature, spectrophotometric determination taken at one hour intervals indicated that I_2 was produced at a constant rate up to 4-5 hours. The observed rates of iodine production are given (in absorbancy units at 4780 Å) in table I.

TABLE I
Rate of Iodine Production in the Photolysis of C_2H_5I

| Length of Photolysis (hours) | Absorbance/hr. for I_2 | μ , einsteins/hr. 3 ml. |
|------------------------------|--------------------------|-----------------------------|
| 4 | 0.0852 | 1.53 |
| 3 | 0.09 | 1.62 |
| 12 | 0.063 | 1.14 |
| Average | 0.088 | 1.59 |

On the basis of the reported absorbancy index of iodine in ethyl iodide of 1280⁽³⁾ l/mole-cm. it can be calculated that the rate of iodine production in the photolysis of ethyl iodide at room temperature with the equipment used is 0.415 microequivalents/

3 ml.-hr. On the basis of this rate of iodine production and the reported quantum efficiency of 0.26⁽⁴⁾ equivalents of iodine produced per quantum of 2537 Å light at room temperature, that light to the cell can be calculated as 1.59×10^{-6} einsteins/hr. The value 1.59×10^{-6} obtained in the present work can be compared with the value 2.27×10^{-6} , 1.85×10^{-6} and 2.52×10^{-6} in the same units reported by Luebbe, and Willard,⁽¹⁾ by Johnston and Willard,⁽⁵⁾ and by Ela and Willard,⁽⁶⁾ respectively, for the same photolysis, using same type of lamp, in the same position with the same current reading.

Photochemical Exchange between C₂H₅I and II¹³¹ in Hydrocarbon Solution at Room Temperature. The exchange of iodine between C₂H₅I and I₂ in the absence of light was performed. 3 ml. of hydrocarbon solution containing 1 mole % of C₂H₅I was placed in the pyrex thimble and degassed. After introduction of I₂ it was sealed off the vacuum line and kept standing at room temperature in the dark for 2 to 10 hours. It then was analyzed to check for any possible dark exchange during the cell filling procedure or during the short period of standing as room temperature. The results obtained in table II are taken as an example.

TABLE I
Dark Exchange between C₂H₅I and II¹³¹ in n-C₄H₁₀

| CCl ₄ layer c/m | SO ₂ layer c/m | Exchange % |
|----------------------------|---------------------------|------------|
| 1312 | 215500 | 0.6 |
| 1910 | 325500 | 0.6 |
| 2350 | 141400 | 1.6* |
| 2800 | 335700 | 0.83 |

It is believed that the percentage exchange has no correlation with the time of standing between the filling of the vessel and analysis and that the exchange takes place during the period of filling the vessel.

The results for the photochemical exchange experiments in hydrocarbons, n-pentane, isopentane and cyclopentane, at room temperature are shown in table III. Johnston's method of treating the data was used and the simple equilibrium exchange law was then used to evaluate the apparent exchange

rate, i.e.,

$$R_0 = 2 \times 2.303 \left(\frac{-\log(1-F)}{t} \right) \times (I_2)_0$$

The fractional exchange was calculated as

$$F = \frac{(c/m \text{ organic}) - (c/m \text{ organic})_{\text{dark}}}{\text{total } c/m}$$

Graphs of $-2 \times 2.303 \log(1-F) \times (I_2)_0/t$ vs. t were drawn and the extrapolated value, R_0 at $t=0$, was obtained.

TABLE II
Photochemical Exchange between C₂H₅I and II¹³¹ in Hydrocarbons at Room Temperature

| Hydrocarbon | (C ₂ H ₅ I) mole % | (I ₂) ₀ × 10 ⁴ mole/l | Time hr. | $\frac{-\log(1-F)}{t}$ hr ⁻¹ | Rate × 10 ⁴ mole/l-hr and ϕ |
|--------------|--|---|----------|---|---|
| cyclopentane | 1 | 5.67 | 1 | 0.074 | 1.99 |
| | 1 | 5.23 | 3 | 0.082 | $\phi=0.37^*$ |
| | 1 | 5.50 | 0.5 | 0.080 | |
| n-pentane | 1 | 5.65 | 4 | 0.077 | |
| | 1 | 5.55 | 4 | 0.094 | 2.6 |
| | 1 | 5.45 | 2 | 0.103 | $\phi=0.51^*$ |
| isopentane | 1 | 5.65 | 1 | 0.104 | |
| | 1 | 7.45 | 1 | 0.095 | 3.3 |
| | 1 | 7.2 | 2 | 0.098 | $\phi=0.62^*$ |
| | 1 | 6.9 | 3 | 0.104 | |

* Quantum yields were calculated on the assumption that the absorbed light intensity was 5.3×10^{-4} einsteins/hr-l.

VI. Discussion

The Origin of Discussion. A C₂H₅I molecule in a hydrocarbon solvent dissociates after absorption of 2537 Å light and C₂H₅ and I formed separate with a 2 ev of kinetic energy. The excess energy will be at once lost in collision with the solvent and the radical and atom will be thermalized at a distance of one or few molecular diameters from each other. We assume that C₂H₅ has lost all their energy in collision with a solvent molecule at a distance (mean free path) from I atom. The radical C₂H₅ now starts motion with equal probability for every direction. The probability for primary recombination⁽⁷⁾ can be expressed by

$$f = \frac{\pi d^2}{4\pi \lambda^2}$$

where d is the molecular diameter. This estimation is intended only to show that the probability of

primary recombination in a condensed system can not be disregarded; it seems reasonable to expect an effect of this kind reaching the order of 10^{-1} . The primary recombination must depend upon the nature of dissociation products (the existence of the least energy-barrier for the recombination will cause the effect to disappear) and of the solvent (on its viscosity) as well as on the absorbed wave length. A great excess energy will permit the dissociation product to find their way through the surrounding wall of the solvent and to put more molecular layers between them before coming to rest. The equilibrium concentration of free radicals in solutions, as compared with a gas, is affected not only by a decreased rate of formation and the possibility of primary recombination but also by an increased probability of secondary recombination after escape from the cage, resulting from the fact that every collision of two radicals in solution is made a triple or multiple collision by the presence of the solvent. Thus the rate constant of secondary recombination in every solution may be greater by the factor 10^3 to 10^4 than it is in a gas at atmospheric pressure.⁽⁷⁾

Now we consider a chemical reaction such that;



This is a possible scheme of photochemical reaction proceeding through the intermediary of free radicals with a quantum yield depending on the competition between exchange reaction (2a) and primary and secondary and recombination (2b). If the reaction (2a) should have no or but a small energy of activation then (2b) will play no role at all in the mechanism of the reaction, since the scavenger I_2 is present in concentration which is many orders of magnitude greater than the equilibrium concentration of free radicals at any practically obtainable intensity of illumination.

The distinction between primary and secondary recombination of radical and atom was not included, since it is not experimentally observable by the technique used in the present work. Added I_2 and I_2 produced by even short irradiation of $\text{C}_2\text{H}_5\text{I}$ in

hydrocarbon are far greater than the steady state radical concentration in the bulk of solution.

Effect of Viscosity of the Solvent. The ratio of the quantum yield for exchange of an atom between $\text{C}_2\text{H}_5\text{I}$ and I_2 in the different hydrocarbons is 1 (cyclopentane): 1.38 (n-pentane): 1.66 (isopentane). Speaking very qualitatively, the data show that rate for the exchange reaction decreases markedly with the idea that the radicals are produced in a cage of solvent molecules and must force their way out if they are to escape recombination with each other. The diffusion coefficient could contribute a rough measure of the ability of radicals to undergo a diffusion displacement after its energy is in thermal equilibrium with its surroundings, and the diffusion coefficient is inversely proportional to viscosity.

Effect of the Concentration of I_2 Added. Luebbe and Willard⁽¹⁾ showed that introduction of I_2 to $\text{C}_2\text{H}_5\text{I}$ prior to photolysis decreases the initial rate of iodine production below the normal rate, but that the rate increases toward normal during photolysis. In the present work added I_2 acted as an effective scavenger in the system and showed the absence of change in the apparent rate of exchange when the I_2 concentration was changed by a factor as great as 2, and the presence of change in the fractional change $-F$ (or $-\log(1-F)/t$). When (I_2) increased, F decreased and conversely for a decrease in (I_2). The data with n-pentane are shown in Table IV.

TABLE IV
Photochemical Exchange between $\text{C}_2\text{H}_5\text{I}$ and I_2 ¹³¹
in n-Pentane at Room Temperature.

| $(\text{C}_2\text{H}_5\text{I})$ mole% | $(\text{I}_2) \times 10^4$ mole/l | F | $-\log(1-F)/t$ hr ⁻¹ | Time hr. | Rate $\times 10^4$ mole/l-hr. |
|---|--------------------------------------|------|------------------------------------|-------------|----------------------------------|
| 1 | 11.9 | 0.11 | 0.05 | 1 | 2.7 |
| 1 | 6.1 | 0.58 | 0.094 | 4 | 2.65 |
| 1 | 2.7 | 0.79 | 0.226 | 3 | 2.8 |

The results indicate that within the sensitivity of experiment the added I_2 affects the rate only by competition with the other I_2 for free radicals not by interference with some independent process such as the primary recombination in the cage.

Effect of Oxygen. Horning and Willard⁽³⁾ showed that addition of O₂ to C₂H₅I prior to radiolysis increased the initial iodine production rate by 2.2 times; the rate decreased toward normal as radiolysis continued. In the present work it was accidentally found in an actinometry run that the initial iodine production was very high, this increase might be due to leakage of air through the cracked surface of reaction cell.

V. Summary

It is the purpose of this section to summarize some of the present work, together with examples from other workers, in the hope that such a summary and interrelation of available information will help to make a better comparison of results and serve as an aid for further work. Table V includes a summary of the results obtained in the present work and those obtained by Ela and Willard⁽⁶⁾ and by Johnston and Willard⁽⁵⁾. This summary shows that the relative caging effectiveness is very closely related to the chain length of the hydrocarbon, from results by Johnston and Willard,⁽⁵⁾ and by Aditya and Willard,⁽⁸⁾ and structure of solvent from results of the present work in the same system.

The difference in quantum yields of n-pentane and isopentane between the present data and that of Ela, and the difference between Ela's n-pentane and that of Johnston's are presumed to be due to the differences in actinometry data, cell position in the cryostat and current and lack of machining in different cells.

The difference between cyclopentane and n-pentane or isopentane is mainly due to the difference in viscosity of the solvent as discussed in a previous section. The difference between n-pentane and isopentane in present work shows a greater ratio

of quantum yield than that expected by the ratio of viscosity, this may be due to rather difference in structure of solvent than viscosity difference.

The agreement between the present data of n-pentane and that of Johnston can be interpreted as due lower difference in the previously described factors between the present work and Johnston's.

TABLE V

| Hydrocarbon | (C ₂ H ₅ I) mole/% | (I ₂) × 10 ⁴ mole/l | Light intensity, einste- in/hr. × 10 ⁴ | ϕ_0 | Viscosity |
|------------------------------------|--|--|---|---------------------|-----------|
| Cyclopentane | 1 | 5.6 | 5.3 | 0.37 ⁽¹⁾ | 0.492 |
| n-C ₅ H ₁₂ | 1 | 5.6 | 5.3 | 0.51 ⁽¹⁾ | 0.289 |
| iso-C ₅ H ₁₂ | 1 | 5.6 | 7.2 | 0.62 ⁽¹⁾ | 0.273 |
| n-C ₆ H ₁₄ | 1 | 8.2 | 7.6 | 0.39 ⁽²⁾ | 0.289 |
| iso-C ₆ H ₁₄ | 1 | 8.5 | 7.6 | 0.41 ⁽²⁾ | 0.273 |
| n-C ₇ H ₁₆ | 1 | 2.2 | 6.2 | 0.53 ⁽³⁾ | 0.289 |
| n-C ₈ H ₁₈ | 1 | 7.9 | 6.2 | 0.46 ⁽³⁾ | 0.294 |
| n-C ₉ H ₂₀ | 1 | 7.2 | 6.2 | 0.37 ⁽³⁾ | 0.386 |
| n-C ₁₀ H ₂₂ | 1 | 5.8 | 6.2 | 0.26 ⁽³⁾ | |
| n-C ₁₀ H ₂₂ | 1 | 5.8 | 6.2 | 0.19 ⁽³⁾ | |

(1): Results obtained in the present work; (2), (3): Results obtained by Ela and Johnston respectively.

References

1. R.H. Ruebbe, Ph. D. Thesis, University of Wisconsin, 1958.
2. R. Hanrahn, Ph. D. Thesis, University of Wisconsin, 1957.
3. E.O. Horning & J. E. Willard, *J. Am. Chem. Soc.* **79**, 2429(1957).
4. E.L. CoChrn, W.H. Hammel & R.R. Williams, Jr., *Ibid.*, **76**, 2445(1954).
5. F. Johnstone and J.E. Willard, "Caging Effect in the Photolysis of C₂H₅I" (unpublished results).
6. S. Ela and J.E. Willard, "Caging Effect in the Potolysis of C₂H₅I" (unpublished results).
7. J. Frank and E.Rabinowich, *Tran. Faraday Soc.*, **30**, 120(1934).