The Photolysis of Iodine, Ethyl Iodide and Hydrogen Iodide

in a Rigid Glass at 77°K

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It has been found that the photolysis of iodine in a hydrocarbon matrix at 77°K does not lead to the formation of iodine atoms. That the photolysis of ethyl iodide depends on the viscosity of the matrix has been confirmed and spectral characteristics of intermediates have been recorded. Identical characteristics were found when HI was photolyzed and it has been shown that HI_3 is not involved.

In a search for molecular species that can be split homolytically by photo-lysis in a glass-forming matrix at the temperature of liquid nitrogen a number of iodine-containing substances have been investigated. The photolysis of iodine, ethyl iodide and hydrogen iodide constitutes the subject of the present paper.

Iodine itself has previously been studied by Norman and Porter [1, 2] and by Sowden and Davidson [3] under similar conditions but with controversial results. Norman and Porter [1] found it possible by photolysis to decolorize a 10^{-3} M iodine solution in a hydrocarbon glass at 86°K and to regain the iodine color during warm-up. On the other hand, Sowden and Davidson [3] found a 10^{-4} M solution to be unchanged even by prolonged irradiation. In a later paper, Norman and Porter [2] described the experimental conditions and results more in detail when using the EPA-matrix (ethanol, ethyl ether and isopentane 2:5:5).

Norman and Porter [2] have also studied the photolysis of EtI in different matrices. These authors suggested that atomic iodine was formed, which is stable at 77°K for several hours in a high-viscosity, "hard" matrix like pure 3-methyl pentane or the mixture 3-methyl pentane, isopentane 3:2, whereas in a low-viscosity, "soft" matrix like pure isopentane diffusional processes lead to the formation of molecular iodine already at liquid nitrogen temperature. Upon warm-up the spectrum of iodine appeared instantly also in hard glasses. In EPA, the authors found that the solid solution irradiated for 1 h remained transparent down to the beginning of absorption by EtI. On warming to room

temperature, the absorption spectrum of iodine developed rather slowly, showing also the absorption bands at 290 and 360 mμ attributed to hydrogen tri-iodide [4]. Norman and Porter concluded that the photolysis of EtI leads to the formation of unknown species, which may be HI. They do not give any corresponding results when hydrocarbon matrices were used.

It was felt to be of interest to repeat the photolysis of ethyl iodide with a differential method on a hydrocarbon matrix and to compare the results with those from experiments performed on hydrogen iodide under identical conditions.

MATERIALS

Iodine used was "Baker analyzed" reagent.

Ethyl iodide, Merck analytical grade, was distilled and the main fraction was found to contain less than 0.05 % of gas-chromatographically detectable impurities.

Hydrogen iodide was prepared directly in a 10^{-3} M hydrocarbon solution by reduction with pure hydrogen of an appropriate amount of iodine in the presence of $10-20$ % by weight of platinum oxide (Adams catalyst [5]).

Matrix hydrocarbons were purified and tested according to standard procedure [6].

Apparatus and Technique have been described elsewhere [7-8].

RESULTS

Iodine. (Fig. 1) Iodine solutions (1.5×10^{-5} to 4×10^{-5} M) * were prepared in three different glasses: two mixtures of isopentane and 3-methyl pentane, 2:3 by volume [2] (matrix C) and 6:1 by volume [9] (matrix A) and a mixture of pentane and *neo*hexane 3:8 by volume [10] (matrix B). The solutions were cooled to liquid nitrogen temperature (curve 1) and irradiated for 60 min (curve 2). All glasses were yellow and fully transparent in the visible region throughout the experiments. The peaks at 19.9 and 23.0 kc. cm^{-1} were clearly discernible both before and after photolysis. In accordance with the results of Sowden and Davidson no decolorization was obtained, and the spectrum changed only slightly or not at all during the irradiation. After warm-up, the original spectrum was obtained, within the error of reproducibility of the instrument (curve 3). On refreezing, however, the spectrum differed slightly from the unirradiated one at 77°K (curve 4).

Ethyl iodide was irradiated at liquid nitrogen temperature in all three matrices given above at concentrations between 10^{-3} and 10^{-4} M. The spectral changes following upon irradiation depended on the viscosity of the matrix **. In the high-viscosity matrix, C (Fig. 2a), the absorption peak at 38.9 kc. cm^{-1} (curve 1) decreased regularly during the initial $15-20$ minutes of photolysis. At the same time the absorption at higher frequencies increased whereas the curve is unchanged at lower frequencies. The curves for different photolysis times cross each other in an isosbestic point at about 42.4 kc. cm^{-1}.

For longer irradiation periods, up to 60 minutes, the absorption increased over the whole UV-region with a recognizable peak at about 23 kc. cm^{-1} (curve 2). This spectrum remained unchanged as long as liquid nitrogen

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* Above *ca.* 10^{-4} M, the solution became turbid upon freezing.
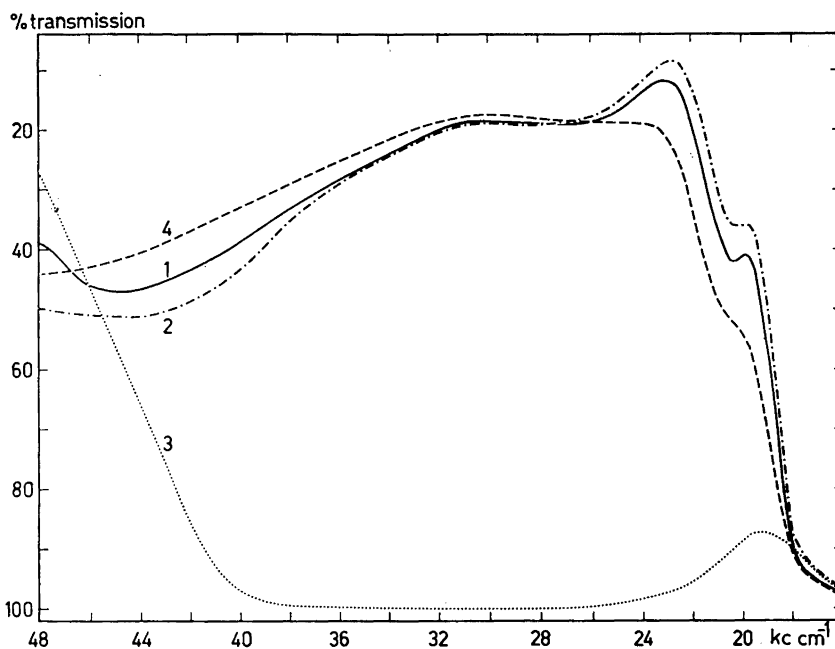** For an experimental study of the viscosity of the different matrices see Ref. [6]

Fig. 1. Spectra of a 3 × 10⁻⁵ M iodine solution in matrix A. (1) before and (2) after 60 min. of photolysis at 77°K, (3) after warm-up to 298°K and (4) after recooling to 77°K.

surrounded the cell. If the sample was slowly warmed up when still in the cell compartment, the following changes in the spectrum occurred:

A weak maximum appeared at 13.9 kc. cm⁻¹, a strong double peak at 25.8 and 27.4 kc. cm⁻¹, respectively, and a peak at 34.4 kc. cm⁻¹ (curve 3). When room temperature was reached the spectrum showed only the presence of iodine: a peak at 19.1 kc. cm⁻¹ and an increased absorption in the far UV-region (curve 4). Refreezing to liquid nitrogen temperature, however, did not result in the spectrum of an iodine solution at 77°K (Fig. 1, curve 1); the absorption below about 30 kc. cm⁻¹ is lower and above this point higher for the irradiated sample than it is for iodine (curve 5). Besides, a new peak appeared at 22.3 kc. cm⁻¹, which might be an indication of the formation of HI_3 (see below).

In the other matrices spectral changes occurred already during irradiation when the cells were surrounded by liquid nitrogen. Fig. 2b, curve 1 shows the absorption of a 0.25 mM EtI solution in matrix A at 77°K. After 5—10 minutes of irradiation a peak developed at 25.8 kc. cm⁻¹ and at about 21 kc. cm⁻¹ (curves 2 and 3). On prolonged irradiation peaks at 27.4 and 34.4 kc. cm⁻¹ developed faster than the 25.8 kc. cm⁻¹ peak, so that the final spectrum at 77°K (curve 4) was similar to that obtained in matrix C. 15 minutes of photolysis of EtI in matrix B gave rise to peaks at 25.6, 27.5 and 34.4 kc. cm⁻¹ and a shoulder at about 21 kc. cm⁻¹ — that is, the same characteristic frequencies as in the chemically different matrices A and C.

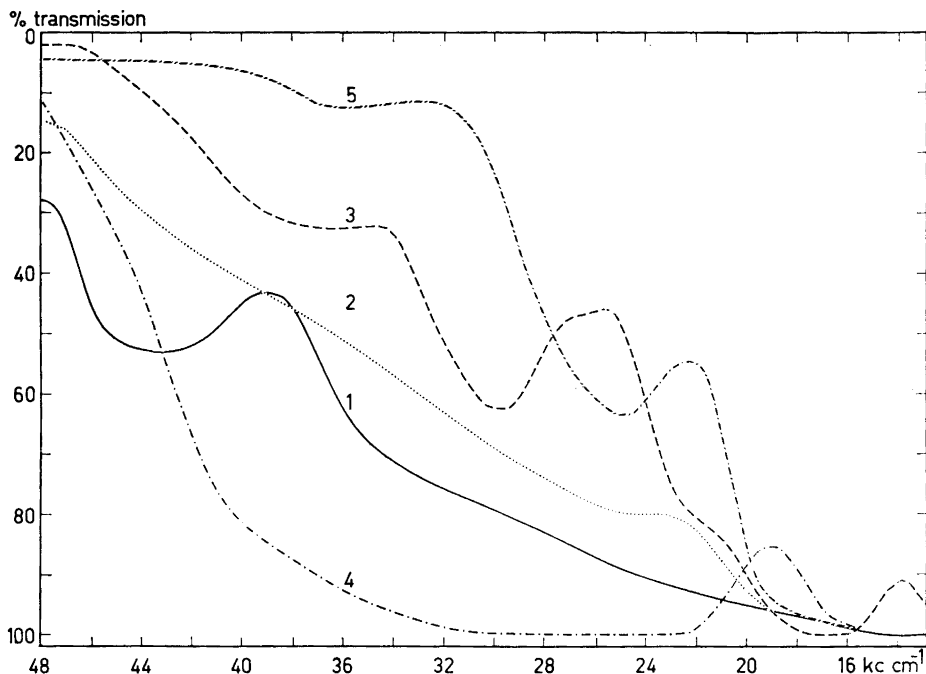% transmission

Fig. 2a. Spectra of a 2.5×10^{-4} M ethyl iodide solution in matrix C. (1) before and (2) after 60 min. of photolysis at 77°K, (3) during warm-up, at approximately 90—95°K, (4) after warm-up to 298°K and (5) after recooling to 77°K.

Hydrogen iodide. At room temperature, hydrogen iodide has an absorption maximum at 37.4 kc. cm^{-1} (Fig. 3) in the hydrocarbon mixtures used (curve 1). At liquid nitrogen temperature this maximum is changed to 36.7 kc. cm^{-1} and a new weaker maximum appears at 32.1 kc. cm^{-1} (curve 2).

Hydrogen iodide was irradiated in matrices A and B at concentrations between 2×10^{-4} and 4×10^{-4} M. In the harder matrix C, only one experiment could be performed as the cells almost invariably broke during photolysis. In both glasses the two HI absorption peaks rapidly decreased upon irradiation; after about 10 min. they had practically disappeared. The changes in spectrum as a result of the irradiation were quite analogous to those obtained with ethyl iodide. Thus, the final spectrum at low temperature was dominated by a peak at 34.4 kc. cm^{-1} and a double-peak at 27.4 and 25.8 kc. cm^{-1} (curve 3). After warm-up the spectrum was again that of iodine (curve 4) and after refreezing the spectrum resembled that of irradiated ethyl iodide under the same conditions, with a peak at 22.7 kc. cm^{-1} (curve 5).

Hydrogen iodide and iodine. (Fig. 4) Solutions were prepared in matrix A containing both hydrogen iodide (about 4×10^{-4} M) and iodine (about 3×10^{-5} M). At room temperature the spectrum showed the absorption of both compounds. At 77°K, however, the spectrum did not consist of super-
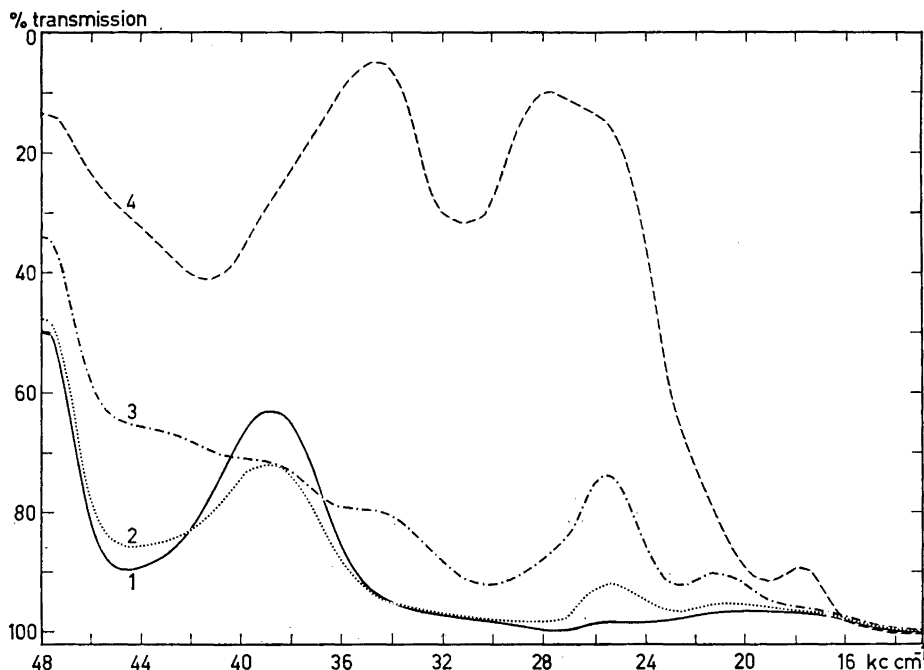
Fig. 2b. Spectra of a 2.5 × 10⁻⁴ M ethyl iodide solution in matrix A at 77°K. (1) before and after (2) 5 min., (3) 12 min. and (4) 30 min. of photolysis.

imposed spectra of hydrogen iodide and iodine (curve 2). The excess HI could easily be identified on a high absorption background with peaks at 36.7 and 32.1 kc. cm^{-1}. Contrary to this the low temperature absorption of iodine in the wavenumber range 28—18 kc. cm^{-1} was absent and a new sharp peak had developed at 22.1 kc. cm^{-1}. Irradiation of this mixture gave the same spectral changes as a hydrogen iodide solution alone (curve 3).

<div align="center">DISCUSSION</div>

Upon freezing the violet iodine-solution in a hydrocarbon mixture solidified to a yellow, transparent glass, the color change being caused by an increase in light absorption for wavenumbers higher than about 20 kc. cm^{-1}. It has been suggested that the cause may be the low solubility of iodine at 77°K. An extrapolation made by Ham [11] led to an order of magnitude of 10^{-11} M and thus the color of the solution should be caused by microcrystals of iodine. Evans [12] has pointed out that the iodine solution may be colloidal and that Norman and Porter [1], who were able to prepare a transparent 10^{-3} M solution of iodine, probably used solvents containing impurities which formed complexes with I_2.
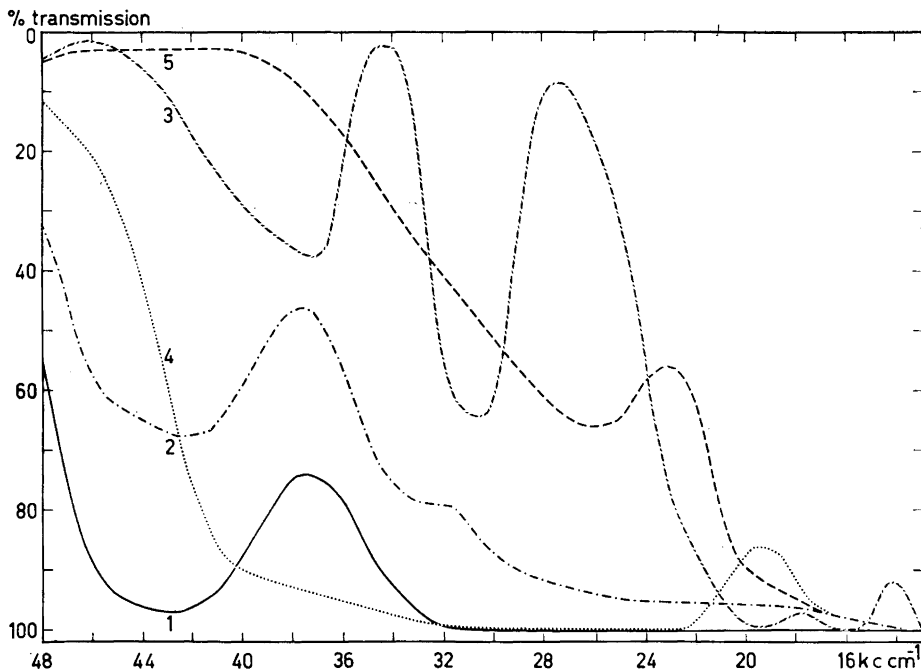
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Fig. 3. Spectra of 1.9 × 10⁻⁴ M hydrogen iodide solution in matrix A. (1) at 298°K, (2) before and (3) after 60 min. of photolysis at 77°K, (4) after warm-up and (5) after recooling to 77°K.

The existence and the reproducibility of the 23.0 and 19.9 kc. cm⁻¹ peaks show that certain complexes between iodine and solvent molecules must be present in all matrix-forming hydrocarbon mixtures and that the peaks probably are superimposed on a continuous background absorption. It may be the presence of complex-forming impurities in the solvents or the formation of contact charge transfer complexes [13, 14] that give rise to the peaks.

From the irradiation experiments it was apparent that iodine did not photolyze under the conditions chosen. The 23.0 kc. cm⁻¹ peak, which did not change very much upon photolysis, disappeared, however, after warm-up followed by refreezing. This could simply be explained by assuming that a type of minor impurity present in both glass-forming mixtures reacts during warm-up.

The absorption curves for HI compared with those for the HI-I_2-mixture clearly demonstrated the existence of a complex between HI and I_2 at 77°K with an absorption peak at 21.9 kc. cm⁻¹. Both the photolyzed solution of HI as well as that of EtI showed the formation of I_2 upon warm-up and the same peak became visible upon refreezing at 22.4 and 22.3 kc. cm⁻¹, respectively (corrected for the background absorption).
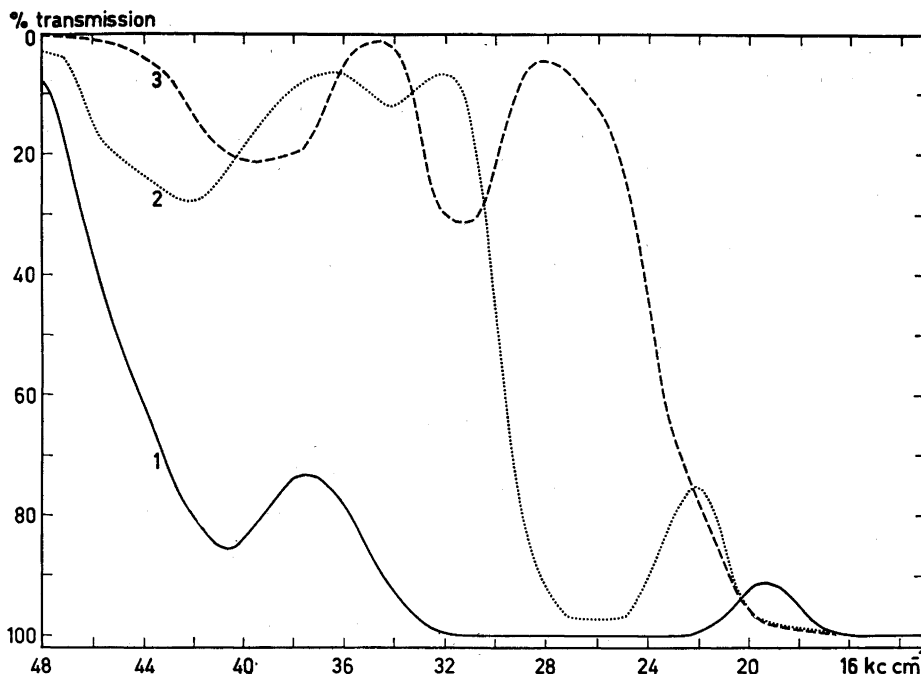
Fig. 4. Spectra of a mixture of 4 × 10⁻⁴ M hydrogen iodide plus 3 × 10⁻⁵ M iodine in matrix A solution. (1) at 298°K, (2) before and (3) after 10 min. of photolysis at 77°K.

In the experiments with EtI the influence of the viscosity of the matrix was clearly demonstrated, confirming the results of Norman and Porter [2]. In the hard matrix, C, the EtI-peak at 38.9 kc. cm⁻¹ diminished continuously during rather short times of photolysis without a simultaneous formation of intermediates, which produce a higher absorption below 42.4 kc. cm⁻¹ than EtI itself. The obvious suggestion is that photolysis occurred during the formation of iodine atoms and ethyl radicals [2]. For longer irradiation periods the continuously increasing absorption when going towards higher wavenumbers might be caused by secondary irradiation processes *.

When the photolyzed EtI solution in matrix C was slowly warmed up the same change occurred as in matrices A and B at 77°K, although distinct differences also were apparent. The spectral changes indicated a sequence of reactions and most probably the formation of more than one intermediate species, showing absorption maxima at 34.4, 27.4, 25.8 and 13.9 kc. cm⁻¹. That the photolysis of HI leads to the formation of the same absorption peaks must

* The optical properties of the solid solutions in the different matrices showed quite a variation at 77°K. EtI in matrix C gave a rather high background absorption (Fig. 2a, curve 1). In spite of this, the spectral changes could very well be reproduced although calculations of extinction coefficients became too uncertain to be of value.

have a profound bearing upon the nature of the intermediate products. It therefore seems that they all are related to iodine-containing intermediates and that they have very little, if anything, to do with the existence of a HI_3 complex (*cf.* Fig. 4). It is of interest, however, to note that the well-known peaks produced by an ethanolic iodine solution, at 34.5 and 27.8 kc. cm^{-1}, have been attributed to HI_3 by Batley [4], and that the 34.4 and 27.4 kc. cm^{-1} peaks obtained when EtI and HI are photolyzed develop simultaneously.

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