

## The Photolysis of Iodine and Ethyl Iodide in Oxygen-free and Oxygen-containing Hydrocarbon Matrices at 77°K

D. TIMM

*Thermochemistry Laboratory,\* University of Lund, Lund, Sweden*

Molecular iodine and ethyl iodide have been photolyzed at 77°K in matrices prepared from both oxygen-containing and completely oxygen-free saturated hydrocarbons. Spectra of the photolyzed solutions have been recorded at 77°K and at successively higher temperatures. Between 77°K and about 140°K unstable intermediate species considered to be iodine atom charge-transfer complexes were found. Moreover, in oxygen-containing hydrocarbons, hydrogen triiodide, or possibly triiodide ions, seem to be formed as transient species.

In a previous paper<sup>1</sup> studies of the photolysis of ethyliodide, hydrogen iodide, and iodine in a hydrocarbon matrix at 77°K were reported. In the course of that work some observations were made that initiated a further study of the spectral changes during warm-up of solid solutions photolyzed at 77°K. This work, which has shown the existence of unstable intermediates, will be described here.

Although many publications may be found in the literature on the photolysis and photochemistry of alkyl iodides and elemental iodine, only a few deal with the detection and identification of unstable iodine containing species.<sup>2-4</sup> In these cases flash photolysis at ambient temperatures was the technique used. The method used in the present work allows the study of single steps in a complex recombination reaction.

It has recently been found in this laboratory that oxygen is an extremely persistent impurity in hydrocarbons.<sup>5</sup> Even the most rigorous purification by standard procedures<sup>6,7</sup> leaves oxygen in the hydrocarbon as indicated by the absorption around 50 kKaysers.\*\* When completely oxygen-free solvents became available, comparative experiments revealed considerable differences in spectral behaviour between oxygen-containing and oxygen-free matrix systems, particularly during warm-up.

\* Sponsored by *The Swedish Natural Science Research Council* and *The Swedish Technical Research Council*.

\*\* kKaysers, in the following kK, is used for  $10^3 \text{ cm}^{-1}$ ; see *J. Opt. Soc. Am.* **43** (1953) 410.

## EXPERIMENTAL

*Photolysis.* The photolysis set-up, consisting of two super high-pressure mercury lamps (900 W each), 35 mm filter cells filled with nickel sulfate solution (285 g  $\text{NiSO}_4 \cdot 6 \text{H}_2\text{O}$  per liter; high wave number cut off limit 45.4 kK) and exchangeable glass filters, has been described previously.<sup>8</sup> The total amount of irradiation has been measured with an uranyl oxalate actinometer; without glass filters it corresponds to  $1.8 \times 10^{17}$  quanta/sec,  $\text{cm}^2$ . The matched filters used in the present investigation were Jena Mainz WG 1, WG 2, WG 4, and WG 7, with high wave number cut off limits 28.9, 31.0, 33.0, and 41.1 kK, respectively. The filters were transparent down to 13 kK.

*Spectrophotometry.* The liquid nitrogen cell compartment, accommodating two  $17 \times 19$  mm quartz cells, used both for photolysis and spectrophotometry, has been described previously.<sup>9</sup> It was used together with a Unicam SP 700 spectrophotometer, recording linearly in optical density. Later experiments were made with one cell only; the reference beam then passed through a 22 mm layer of liquid nitrogen compared with two 1 mm layers in the sample beam. The absorption in this extra 20 mm of liquid nitrogen was found to be negligible in the spectral region investigated (51–13 kK).

*Experimental procedure.* The filling, outgassing and sealing of the quartz cells, as well as general procedures, have been described previously.<sup>8</sup> The experiments with oxygen-free hydrocarbons were performed in a modified type of cell (see Ref. 5), which allowed the purity of the degassed hydrocarbon to be tested spectrophotometrically before the solute was added. For this purpose a break-seal ampoule containing the sample of iodine or ethyl iodide was sealed to the quartz cell. After breaking the seal the content of the ampoule was distilled over to the hydrocarbon mixture in the cell.

Following photolysis at 77°K, spectra of the photolyzed samples were taken at 77°K, at a number of intermediate temperatures, and at room temperature. Intermediate temperatures were obtained by pumping off enough liquid nitrogen to lower the nitrogen level below the sample cell. The temperature of the cell then started to increase, 150°K being reached after 73 min and 273°K after about 250. Spectra were taken every 10 min during the warm-up period. For comparison, spectra at different temperatures were also taken of the sample prior to photolysis. The temperature-time curve was determined from independent calibration experiments using a cell with a built in platinum resistance thermometer (Heraeus 100 ohm,  $12 \times 5$  mm). The time zero was taken to be the moment when the liquid nitrogen level left the lowest part of the sample cell. The resistance thermometer was calibrated at  $-182.97^\circ\text{C}$  (oxygen point), at  $-78.51^\circ\text{C}$  (solid  $\text{CO}_2$  at 1 atm.) and at  $0.00^\circ\text{C}$  (ice point), and was used together with a Mueller G 1 bridge (Rubicon type 1551). The temperature-time curve could be reproduced to within a degree. The recording time for a spectrum between 51 and 13 kK was *ca.* 5 min and the temperature was taken as the mean over the recording period.

All concentrations given in this paper refer to room temperature. The actual concentration at 77°K is greater by a factor of 1.31 for solutions in matrix A and 1.30 for solutions in matrix C (see below).

*Materials. Iodine:* Merck resublimed iodine was resublimed once and stored over concentrated sulfuric acid. In experiments with oxygen-free hydrocarbons the sample of iodine was transferred to a break-seal ampoule, which was then outgassed, gently at room temperature and thoroughly at 77°K, before it was sealed under vacuum.

*Ethyl iodide:* Merck ethyl iodide ( $n_D^{20} = 1.5136$  compared with 1.51369 by Vogel<sup>10</sup>) was used without further purification, as GLC indicated a purity of better than 99.95 % (two different stationary phases were used). The ethyl iodide, which was also added from a break-sealed ampoule, was outgassed in the ampoule by repeated freezing under vacuum, pumping and thawing.

*Hydrocarbons:* Isopentane and 3-methylpentane (Phillips Petroleum Company, techn. grade) were carefully purified by treatment with sulfuric acid, fractional distillation, and adsorption on silica gel, and tested, all according to the procedure described by Rosen-gren.<sup>7</sup> Oxygen-free hydrocarbons were obtained using the procedure described by Nilsson.<sup>8</sup>

The matrix forming mixtures used in this work were:

matrix A: 6 parts isopentane + 1 part 3-methylpentane<sup>11</sup>  
matrix C: 2 parts isopentane + 3 parts 3-methylpentane.<sup>12</sup>

## RESULTS

*Ethyl iodide in oxygen-free hydrocarbons.* A 2 mM solution of ethyl iodide in matrix C (optical density/cell length at 52.0 kK  $0.02 \text{ cm}^{-1}$ , at 50.0 kK  $0.01 \text{ cm}^{-1}$ ; these values were measured without reference, but corrected for absorption in the quartz cell) was photolyzed at 77°K with WG 7 filters. Spectra were recorded after 5, 10, and 20 min of photolysis. As a result of the photolysis the following changes were observed: 1) the absorption of ethyl iodide at 39.0 kK decreased; 2) between 45 and 51 kK an absorption appeared, which increased towards the high wave number limit without reaching a maximum; 3) two small absorption bands appeared at 25.5 and 21.2 kK, respectively (Fig. 1).

The decrease in ethyl iodide absorption followed closely, as expected, a first order decay reaction.

A simple relation between photolysis time and increase in absorption could be found neither in the 45–51 kK range nor for the 25.5 and 21.2 kK peaks.

When the photolyzed sample was allowed to stand at 77°K for 60 min, the following spectral changes could be observed: the 25.5 and 21.2 kK peaks had grown to four and two times their original size, respectively, and a small shoulder around 33 kK had developed. The liquid nitrogen was then pumped

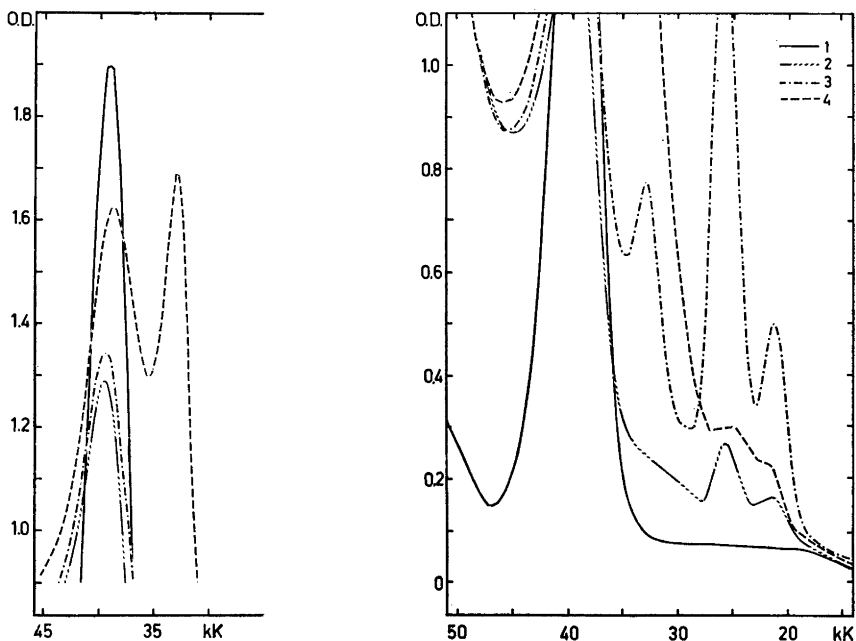


Fig. 1. 2.1 mM ethyl iodide solution in oxygen-free matrix C: (1) before, (2) after 20 min of photolysis at 77°K; (3) at 85°K, (4) at 91°K (after 20 min of photolysis).

off and the temperature was allowed to rise slowly. Spectra were recorded first at 81°K and at 85°K. The only changes compared with the spectrum at 77°K were increased absorption intensities at 33, 25.5, and 21.2 kK. The next spectrum was recorded at 91°K, which is the softening temperature of the matrix used.<sup>7</sup> At this temperature the absorptions at 25.5 and 21.2 kK had almost disappeared, while the band around 33 kK had increased strongly (Fig. 1, curve 4; the apparent increase of the EtI band is caused by the background of the 33 kK band). Table 1 summarizes the intensities of the absorption bands at 21.2, 25.5, and 33.0 kK at different temperatures in a typical experiment.

Table 1. Intensities at different temperatures of unstable absorption bands formed in the photolysis of ethyl iodide.

Spectrum recorded at	Optical densities at		
	21.2	25.5	33.0
77°K, immediately after 20 min of photolysis	0.07	0.13	0.01
77°K, 60 min       »   »   »       »	0.15	0.51	0.04
81°K	0.21	0.69	0.08
85°K	0.29	0.98	0.29
91°K	0.06	0.05	1.31

During the subsequent temperature rise the 33.0 kK peak decreased and at 138°K it had disappeared. It was replaced by an increase in the general absorption level between 18 and 36 kK, which was found to be characteristic of precipitated molecular iodine. This background absorption falls slowly as the temperature and thus the solubility of iodine increases; at 248°K the background had reached its original level.

The room temperature spectrum showed the absorption of remaining ethyl iodide, molecular iodine with maximum at 19.2 kK, and an increasing absorption towards higher wave numbers starting at about 41 kK. The latter has been attributed to charge-transfer during collision between iodine and the hydrocarbons.<sup>13</sup> Presumably, alkene formed in the photolysis contributes to the absorption in this region.

When the photolyzed solution was recooled to 77°K, besides the regular shift of the iodine peak from 19.2 to 21.8 kK, an absorption band appeared with maximum at 32.7 kK. This probably belongs to a charge-transfer complex between iodine and alkene (see Discussion).

When the recooled sample was photolyzed again the scheme described above was followed. A new feature in the spectrum arose, however, from the presence of the iodine-alkene complex. This was readily photolyzed resulting

in the typical triplet around 44.5 kK which will be discussed later (see Molecular iodine).

*Ethyl iodide in hydrocarbons containing small amounts of oxygen.* When the procedure described above was repeated with matrix C containing a small amount of oxygen (optical density/cell length at 52.0 kK  $0.10 \text{ cm}^{-1}$ ; at 50.0 kK  $0.06 \text{ cm}^{-1}$ ) no difference in spectral behaviour was observed until the softening temperature,  $91^\circ\text{K}$ , was reached. At this temperature, besides the alkene-iodine complex at 33.0 kK, an additional absorption with maximum at 45.8 kK appeared. When the temperature reached  $103^\circ\text{K}$  both the 33.0 and the 45.8 peaks disappeared, but instead of precipitation of iodine the well-known triiodide bands at 34.5 and 28.0 kK were formed (Fig. 2). These were stable until the temperature reached  $136^\circ\text{K}$ , when molecular iodine started to fall out. It was, however, dissolved again at  $191^\circ\text{K}$  with a subsequent increase in the intensity of the triiodide bands. During the following temperature rise these bands decreased gradually, resulting in the visible iodine absorption with maximum at 19.2 kK. Solutions with oxygen content higher than specified above behaved analogously, although the iodide and triiodide bands were more intense.

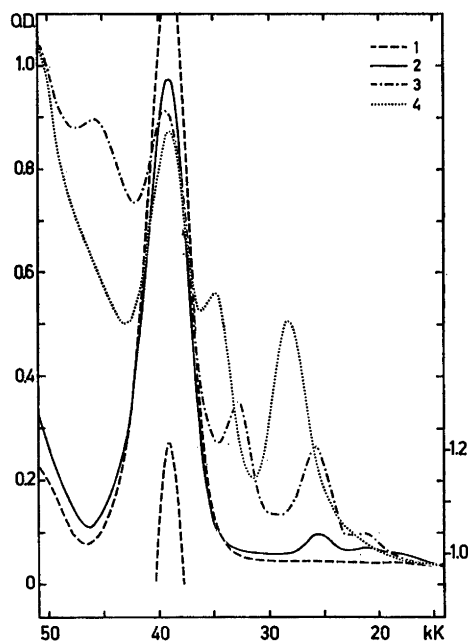


Fig. 2. 1.4 mM ethyl iodide solution in oxygen-containing matrix C: (1) before, (2) after 10 min of photolysis at  $77^\circ\text{K}$ ; (3) at  $89^\circ\text{K}$ , (4) at  $109^\circ\text{K}$  (after 10 min photolysis). The right scale refers to the upper part of curve (1).

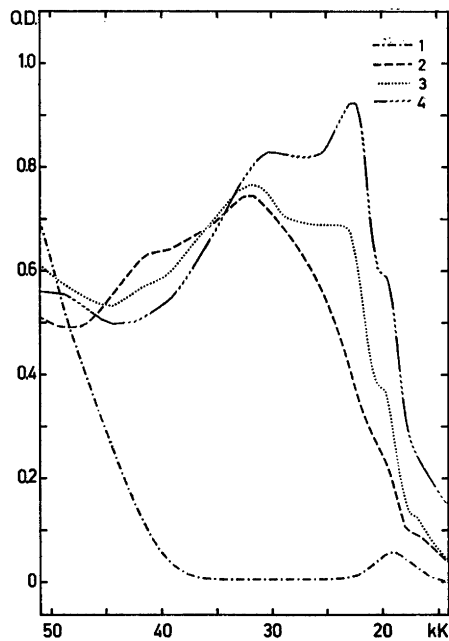


Fig. 3. 0.04 mM iodine solution in oxygen-free matrix C: (1) at  $295^\circ\text{K}$ ; (2), (3), and (4) at  $77^\circ\text{K}$  obtained by cooling at high, intermediate and low rate, respectively.

In oxygen-free as well as in oxygen-containing samples the room temperature spectra after photolysis showed only absorption due to remaining ethyl iodide and molecular iodine. However, the iodine formed corresponded only to a fraction of the photolyzed ethyl iodide. In order to find out whether the iodine lacking existed as hydrogen iodide, the photolyzed samples were opened and shaken with air to quantitatively oxidize hydrogen iodide to iodine.<sup>14</sup> Subsequent spectrophotometric determination of iodine gave, within a few percent, the value demanded by the material balance.

The fraction of photolyzed ethyl iodide which appears as iodine, increases with photolysis time, as shown in Table 2 for oxygen-free samples. This is to

Table 2. Relation between iodine produced and ethyl iodide decomposed as function of photolysis time in the photolysis of ethyl iodide.

Photolysis time (min)	I <sub>2</sub> in percent of photolyzed C <sub>2</sub> H <sub>5</sub> I
10	6
20	9
60	22

be expected since secondary photolysis of hydrogen iodide also produces molecular iodine.<sup>1</sup>

In oxygen-containing solutions the amount of iodine produced is greater since hydrogen iodide is already oxidized before the cell is opened to air.

*Molecular iodine in oxygen-free hydrocarbons.* Iodine solutions in oxygen-free hydrocarbon mixture C (optical density/cell length at 52.0 kK 0.01–0.02 cm<sup>-1</sup>; at 50.0 kK <0.01 cm<sup>-1</sup>) in concentrations between 0.01 and 0.10 mM were cooled to 77°K. Over the whole concentration range the solutions at 77°K appeared transparent by visual inspection. The spectrum revealed, however, that even in the most diluted solution iodine was precipitated, as shown by a general absorption background between 51 and 18 kK of 0.2 optical density units or higher. The absorption could be changed merely by cooling the same solution in the sealed UV-cell at different rates which apparently lead to the formation of iodine crystals of different sizes and distributions (Fig. 3).

Superimposed on this background absorption was found the absorption of iodine in the 22 kK region and usually a shoulder at 19 kK, which is the absorption frequency of iodine at room temperature, was also present. In some samples a small peak (optical density *ca.* 0.05) around 33 kK appeared at liquid nitrogen temperature, probably belonging to a charge-transfer complex between iodine and an unidentified impurity, which was present in much lower concentration than the iodine (about 1:20).

If the unphotolyzed, iodine containing matrix was warmed up, the background absorption started to decrease at about 135°K, and simultaneously the

visible iodine band at 19.2 kK increased, both changes being due to dissolution of precipitated iodine.

Photolysis experiments at 77°K of iodine solutions in hydrocarbon mixture C were carried out with and without WG 7 filters. No spectral changes were observed during or after as much as 120 min of photolysis with WG 7 filters. Warming to room temperature and recooling to 77°K resulted in the same spectrum as before photolysis. When no filter was used the spectrum of the photolyzed sample was still unchanged after photolysis. After warming to room temperature and recooling the photolyzed sample to 77°K, however, an absorption at 33 kK appeared on top of the general absorption. The photolysis time necessary to produce a certain intensity of this absorption seemed to depend on the absorption level in the region above 40 kK, high absorption being favourable. In such a case, an optical density of 0.6 was obtained after 60 min of photolysis (Fig. 4). This absorption band was easily destroyed by photolysis with or without WG 7 filters, the intensity being reduced to half its value in about 3 min. The disappearance of the 33 kK peak was followed by the appearance of a new absorption system consisting of three peaks at 43.0, 44.4, and 45.8 kK with a constant intensity ratio 1:1.4:1.1 (corrected for background absorption). The intensity of these bands depended on the intensity of the 33 kK band from which they were derived, the ratio between corresponding absorption of the 33 and the 44.4 kK bands being  $2.6 \pm 0.2$ . The new bands started to decrease at 91°K and had almost disappeared at 102°K.

When a sample, in which the 33 kK band had been produced in the above manner, *i.e.* photolysis, warming and recooling to 77°K, was warmed without further photolysis, the band decreased gradually and had disappeared at 134°K.

The room temperature spectrum after photolysis without glass filters showed a slight decrease in the iodine absorption at 19.2 kK and an increase between 30 and 40 kK. This increase was always found when iodine and

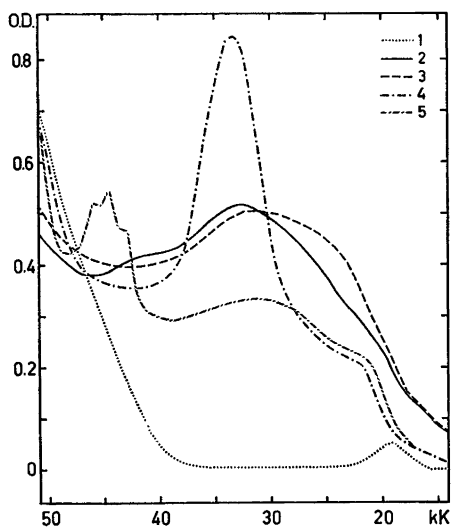


Fig. 4. 0.03 mM iodine solution in oxygen-free matrix C: (1) at 295°K; at 77°K, (2) before and (3) after 60 min of photolysis without glass filters; (4) after warming and recooling to 77°K; (5) after 30 min of photolysis without glass filters at 77°K.

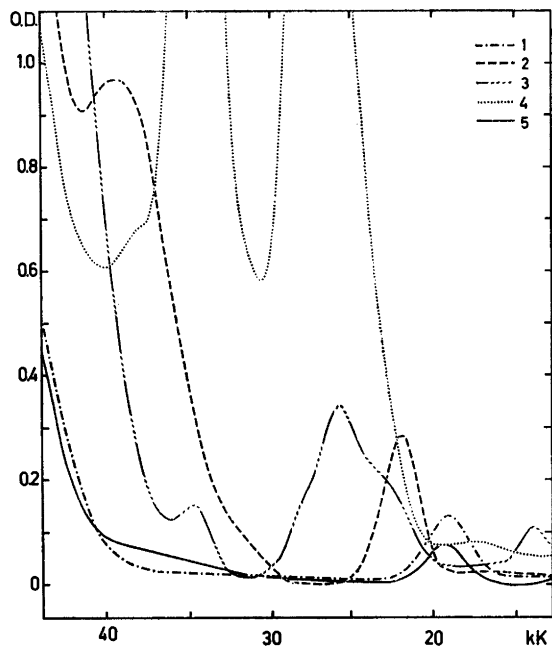


Fig. 5. 0.08 mM iodine solution in oxygen-containing matrix C: (1) at 295°K; at 77°K, (2) before and (3) after 120 min of photolysis with WG7 filters; (4) at 96°K; (5) at 295°K after 120 min of photolysis.

hydrogen iodide were present simultaneously. Also, a very weak shoulder appeared around 45 kK.

*Molecular iodine in oxygen-containing hydrocarbons.* Iodine solutions in hydrocarbon mixtures A and C in concentrations from 0.04 to 0.08 mM were prepared with hydrocarbons which had not been treated according to Nilsson's method for removing "complexed" oxygen.<sup>5</sup> As these experiments were performed before the "break-seal ampoule technique" came into use, the oxygen absorption of the degassed solutions could not be measured due to the high iodine absorption around 50 kK.

Room temperature spectra of these solutions consisted of the visible iodine absorption at 19.2 kK and the high frequency absorption starting at about 40 kK (Fig. 5). On cooling to 77°K the visible absorption was shifted to 21.8 kK, and a new absorption band appeared around 39 kK on the broadened background of molecular iodine. The intensity of this band was proportional to the iodine concentration ( $\epsilon = 3300 \text{ M}^{-1}\text{cm}^{-1}$  as calculated from the iodine concentration).

The spectral changes produced by intermittent photolysis with WG 7 filters for up to 120 min and during the following warm-up are summarized in Table 3 for a typical experiment.



Table 3. Intensities of the absorption bands occurring in the photolysis of 0.08 mM I<sub>2</sub> in oxygen-containing hydrocarbon matrix C.

Spectrum recorded at	Optical densities at							
	13.7	19.2	21.8	23	25.5	28.0	34.5	39
Room temperature	—	0.12	—	—	—	—	—	—
77°K, before photolysis	—	—	0.28	—	—	—	—	0.46
77°K, 10 min »	0.02	—	—	0.11	0.11	0.03	0.07	—
77°K, 60 min »	0.055	—	—	0.05	0.24	0.05	0.10	—
77°K, 120 min »	0.08	—	—	0.03	0.34	0.05	0.11	—
86°K	0.07	—	—	0.03	0.32	0.13	0.25	—
96°K	—	—	—	—	—	1.9	~3	0.03?
102°K	—	—	—	—	—	1.6	~2.5	0.07
Room temperature	—	0.08	—	—	—	—	0.02	0.04

The spectrum of the photolyzed sample remained unchanged as long as the cell was surrounded by liquid nitrogen. When the sample was warmed, a profound change in the spectrum occurred at 91°K, the softening temperature of the matrix. The small triiodide bands at 28.0 and 34.5 kK started to increase, while the 25.5 and 13.7 kK bands started to decrease, as shown in Table 3. During the following temperature rise the triiodide bands decreased gradually under simultaneous development of the visible iodine absorption.

The room temperature spectrum after photolysis showed a decrease in molecular iodine and a slight increase in the absorption between 30 and 40 kK.

When the same experiment was made in matrix A the result was somewhat different in that prolonged photolysis produced appreciable absorption around 28 and 34.5 kK already at 77°K. After 60 min of photolysis the intensities at the maxima were 0.32 and 0.44, respectively. This is easy to understand as the softening temperature of this matrix is about 83°K<sup>7</sup> compared with 91°K for matrix C. The small temperature rise during irradiation is obviously sufficient to take the matrix close to its softening temperature. From this it is apparent that the reactions resulting in triiodide depend on the viscosity of the matrix.

The spectral changes during warm-up proceeded in the same manner as in matrix C with a rapid increase of the triiodide bands at the softening temperature.

Samples of iodine in matrix C were also photolyzed without glass filters, which gave the same results as with WG7 filters but at shorter photolysis times. With WG 1 filters, which together with the nickel sulfate filter solution transmitted only between 16.5 and 22.5 kK, the spectrum was completely unchanged after 60 min of photolysis, and spectra taken during warm-up and after recooling were identical with those of an unphotolyzed sample at the same temperature.

In order to find the lowest photolysis frequency which produced the effects described above, photolysis experiments were carried out with WG 2 and WG 4 filters. When WG 2 filters were used, 120 min of photolysis was com-

pletely ineffective. On the other hand, 60 min of photolysis with WG 4 filters gave the usual changes with small triiodide bands after photolysis, which increased rapidly when the sample reached the softening temperature of the matrix.\*

The lowest active frequency obviously lies between 31.0 and 33.0 kK corresponding to an energy greater than 89 kcal/mole. This value probably includes activation energy of secondary reactions (see Discussion), since the photodissociation of iodine requires not more than 58 kcal/mole.<sup>15</sup> The absence of photolytic effects in photolysis with WG 1 and WG 2 filters may therefore be due to the operation of the cage effect, in that all iodine atoms recombine within the matrix cage without giving spectrophotometrically detectable secondary reaction products.

### DISCUSSION

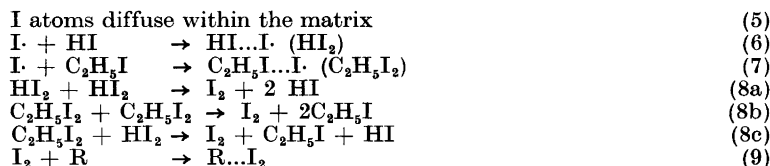
*Photolysis of ethyl iodide.* In the photolysis of ethyl iodide in the gas phase,<sup>16</sup> in the liquid state and in solution<sup>17</sup> and in solid nitrogen at 20°K,<sup>18</sup> the primary step is proposed to be the homolytic splitting of the ethyl iodide into an ethyl radical and an iodine atom. The following steps differ depending on the different experimental conditions.

To account for the spectral behaviour of the ethyl iodide observed in the present work during and after photolysis, the following reaction sequence, essentially analogous to that reported by Bass and Pimentel,<sup>18</sup> is suggested:



All these reactions can take place in the matrix cage.\*\*

To account for the experimental observations during warm-up and on recoiling the following steps are proposed:



Reaction (2) occurs between an ethyl radical and the cage wall (RH<sub>2</sub> stands for isopentane and 3-methylpentane). An analogous reaction has been confirmed by Flournoy and Judeikis,<sup>20</sup> who by EPR showed the formation

\* Development of the triiodide bands is a very sensitive criterion for photolytic effect because of their high molar extinction coefficients of 2.6 and  $4 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$ .

\*\* Luebbe and Willard,<sup>19</sup> who photolyzed pure ethyl iodide at 93°K, concluded from kinetic results that HI is formed in the reaction  $\text{C}_2\text{H}_5\text{I}^* \rightarrow \text{C}_2\text{H}_4 + \text{HI}$ . In the present case this reaction cannot be important, since no charge-transfer absorption attributable to an ethene-iodine complex was found. According to the high ionization potential of ethene this absorption should lie at considerably higher wave number than the observed alkene complex.

of methylcyclohexyl radicals in the photolysis of methyl iodide in a methylcyclohexane glass.

The energy of the ethyl radical can be estimated as follows: Breaking of the  $C_2H_5-I$  bond requires 51 kcal/mole.<sup>21</sup> If the iodine atom in reaction (1) is formed in the excited  $^2P_{1/2}$  state, as in the photolysis of methyl iodide,<sup>22</sup> a further 22 kcal/mole are needed for the excitation of the iodine atom. This leaves an excess energy of at least 38 kcal/mole for radiation absorbed at  $\nu_{max} = 39.0$  kK (corresponding to 111 kcal/mole). This energy is partitioned between the iodine atom and the ethyl radical with at least 31 kcal/mole as translational and possibly vibrational energy on  $C_2H_5\cdot$  (conservation of momentum). Therefore, from energy considerations, the ethyl radical should be capable of abstracting supposedly a tertiary hydrogen atom, since the activation energy of this reaction should not exceed 10 kcal/mole.\*

Reaction (3) will occur to some extent, but the accumulation of pentyl and hexyl iodide will be prevented by secondary photolysis.

Finally, reaction (4) accounts for the formation of alkene and hydrogen iodide.

As a result of reactions (1)–(4) the only observable spectral changes are the decrease of the ethyl iodide peak at 39.0 kK and the appearance of the low wave number side of the vacuum-UV alkene absorption, starting at about 46 kK. The ethane has no absorption in the quartz UV region, and the absorption of hydrogen iodide can probably not be detected in the presence of ethyl iodide.\*\*

In order to explain the formation of molecular iodine after photolysis and warming, it has to be assumed that a certain amount of the iodine atoms formed in reaction (1) escapes the cage. This is indicated by step (5). However, no absorption attributable to iodine atoms was found in the spectral region investigated.

In the gas phase the lowest possible absorption frequency of the iodine atom lies at 48.5 kK (private communication from L. Minnhagen; cf. Ref. 26 which gives the emission spectrum of atomic iodine). Unfortunately, the absorption of the alkene formed in reaction (4) increases strongly in this region at 77°K,  $\log \epsilon$  being 1.3 at 48 kK and 2.8 at 49 kK,<sup>27</sup> which may therefore mask a possible iodine absorption.

When kept at a constant temperature of 77°K the absorption of the photolyzed sample slowly changes. The development of the 25.5 and 21.2 kK peaks seems to be the result of a diffusion controlled reaction, which is accelerated when the temperature is raised. Amongst the species present after photolysis the iodine atom is the only one which should be able to diffuse appreciably. If this is so, the peaks should be attributed to one or two intermediate species containing at least one iodine atom. The peaks disappear almost instantaneously when the softening temperature of the matrix is

\* The activation energy of abstraction of a tertiary hydrogen atom by methyl radicals lies between 7.6 and 7.9 kcal/mole,<sup>23</sup> and with ethyl radicals the activation energy is expected to be only slightly higher.<sup>23</sup>

\*\* The absorption of hydrogen iodide in non-polar solvents like hydrocarbons seems to be controversial at the present time.<sup>1,24,25</sup>

reached, that is, the species decompose when the whole matrix becomes mobilized.\* An obvious suggestion is that one or two charge-transfer complexes are formed with an iodine atom, the latter serving as the acceptor due to its high electron affinity. As the donor we can choose between the following compounds:

1) A saturated hydrocarbon. This is not very likely, as diffusion would not be necessary for the formation of the complex.

2) An alkene. Photolysis of molecular iodine in the presence of excess. If 4-methyl-pentene-2 gave no unstable absorption of the type discussed here on this case, the conditions should be favourable for formation of an iodine atom-alkene complex. Therefore, none of the two bands obtained in the ethyl iodide photolysis should be due to such a complex.

3) Ethyl iodide. Of the two bands the one at 21.2 kK was found to be small or zero when the concentration of remaining ethyl iodide was small or zero. On the other hand, the intensity of the 25.5 kK band was not influenced by the concentration of remaining ethyl iodide. This indicates, that the 21.2 kK peak could be due to a complex  $\text{EtI}\cdots\text{I}$ .

In the photolysis of molecular iodine a peak appeared at 25.5 kK, whereas a peak was never observed around 21 kK. In this case no spectral or GLC evidence was found for the presence of any alkyl iodide. Provided the peaks at 25.5 kK obtained from  $\text{EtI}$  and  $\text{I}_2$  have the same origin, they should therefore not be caused by a complex between iodine atom and ethyl iodide.

4) Hydrogen iodide. It has already been pointed out that the 25.5 and 21.2 kK bands obtained in the low-temperature photolysis of ethyl iodide increased as the result of a diffusion-controlled reaction. When molecular iodine was photolyzed at 77°K a peak at 25.5 kK appeared already *during* photolysis. (In this case a 21.2 kK band has never been observed.) If the 25.5 kK bands in both cases are caused by the presence of a complex  $\text{HI}\cdots\text{I}$ , the difference in behaviour is easy to explain. In the photolysis of iodine the reaction within the cage following homolytic splitting of the iodine molecule is a hydrogen abstraction. This leads to the simultaneous presence of one hydrogen iodide and one iodine atom within the cage. The complex  $\text{HI}\cdots\text{I}$  can therefore be formed directly upon photolysis. When ethyl iodide is photolyzed, only one iodine atom can be found in each cage, and the formation of the complex  $\text{HI}\cdots\text{I}$  requires the diffusion of an iodine atom or a hydrogen iodide molecule. In consequence, the 25.5 kK band does not increase while standing at 77°K when produced by photolysis of iodine, contrary to what happens to this band after photolysis of ethyl iodide.

The formation of the two charge-transfer complexes is indicated by reaction (6) and (7). These are, of course, equilibrium reactions which, at low temperature, are shifted to the extreme right.

Gover and Porter <sup>4</sup> have reported the formation of unstable species in room temperature flash photolysis of molecular iodine dissolved in a number of solvents. They attributed the unstable absorption to charge-transfer complexes between iodine atoms and the solvent molecules. In all cases where a distinct

\* It is of considerable interest to note that these reactions occur at the same temperature as there is a rapid decrease in the macroscopic property, viscosity.<sup>7</sup>

maximum was found in hydrogen containing solvents (except for aromatics), the maximum lay between 3900 and 4000 Å (25.6–25.0 kK) although the ionization potentials of the solvents varied as much as from 9.3 to 12.6 eV. Therefore, it cannot be excluded that all the observed bands are due to the same complex between atomic iodine and hydrogen iodide.\* It is interesting to note, that in the case of ethyl iodide as the solvent Gover and Porter obtained two peaks with maxima at 25.8 and 20.4 kK, *i.e.* close to the unstable peaks reported in the present work.

From the results of experiments mainly on aromatic donors, and from theoretical considerations, Person<sup>28</sup> has derived numerical values of the constants in the expression relating  $\nu_{\max}$  of charge-transfer complexes to the ionization potentials of the donors, when atomic iodine is the acceptor. The ionization potentials for the donors suggested in the present work, HI and EtI, are 10.38 and 9.33 eV, respectively.<sup>29</sup> These values, together with the constants of Ref. 28\*\* when used in the relation mentioned above, yield absorption maxima of 26.3 and 20.7 kK; this is in fair agreement with the observed unstable absorption maxima at 25.5 and 21.2 kK.

The disappearance of the 25.5 and 21.2 kK absorption peaks at the softening point of the matrix can be explained in terms of iodine atom recombination. Collisions between the iodine atom charge-transfer complexes, which are inhibited as long as the matrix is hard, lead to the formation of molecular iodine, as indicated by reactions (8a)–(8c).

Obviously the iodine formed is complexed by the alkene produced in reaction (4), since the disappearance of the iodine atom complexes is accompanied by the appearance of the typical alkene-iodine charge-transfer complex with absorption maximum at 33.0 kK. The intensity of this band is 1.28 optical density units, which results in an  $\epsilon$  value of about 13 000 M<sup>-1</sup>cm<sup>-1</sup> as calculated from the iodine concentration present when the solution is taken to room temperature. This value lies in the range of data for alkene-iodine complexes reported in the literature.<sup>30</sup> The disappearance of the 33.0 kK band during warm-up is due to dissociation of the weak charge-transfer complex as the temperature increases (see below).

With an oxygen-containing matrix the scheme described above is followed until the matrix softens, when an absorption with maximum at 45.8 kK appears as well as that of the alkene-iodine complex. Absorption in this region is characteristic of iodide ions in polar solvents, as for example in water at 44.2 and in butanol at 45.8 kK.<sup>31</sup> It is also obtained by dissolving hydrogen iodide in polar solvents such as ethyl ether with absorption maximum at 44.1 kK,<sup>24</sup> but not in saturated hydrocarbons.<sup>1,24</sup> As the temperature goes up further, both the alkene complex and the “iodide ion” absorptions are replaced by the well-known “triiodide” bands at 34.5 and 28.0 kK. This would be expected if one accepts the existence of both iodide ions and molecular iodine at the lower temperature.

Since the absorption at 45.8 kK and the “triiodide” bands are found only in the oxygen-containing matrix, it is reasonable to assume, that the photolysis

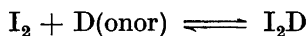
\* The variation of the peak maximum is not unreasonable regarding the differences in solvent polarity.

\*\* The value for  $S$ , the overlap integral should be taken as 0.1 eV for these weak complexes.

produces small amounts of oxygen-containing polar molecules.<sup>5</sup> At low temperatures these molecules remain at the place of their formation, *i.e.* near the polar ethyl iodide and its photolysis products, since it is likely that before photolysis at 77°K, oxygen molecules are close to polar molecules. Thus ionic species could be stabilized by local excess of polar molecules as long as the temperature is low enough to prevent diffusional mixing. Accordingly, the "triiodide" bands disappear when the temperature rises, followed by precipitation of molecular iodine.\*

There is another possible explanation for the observed spectral changes. The "triiodide" bands and the absorption in the iodide region may not require the presence of separated ions, but can also arise from polarized species. Thus, these spectra should be obtained if the polar, oxygen-containing molecules formed by photolysis, produce only an intramolecular charge-transfer in hydrogen iodide and hydrogen triiodide.

*Photolysis of molecular iodine.* When iodine solutions prepared with oxygen-free hydrocarbons were cooled to 77°K, iodine precipitated in all the concentrations investigated. This shows that the solubility of iodine in pure saturated aliphatic hydrocarbons at 77°K is less than 10<sup>-5</sup> M. From solubility data in the temperature range 0–50°C Ham<sup>32</sup> obtained by extrapolation a value of 10<sup>-11</sup> M for the solubility of iodine in heptane at 77°K; this is at least not contradicted by the present observations. If, however, the hydrocarbon contains impurities which form charge-transfer complexes with iodine, the solubility at low temperatures seems to depend on the concentration of the impurity. This is true, of course, only if the impurity is soluble at low temperatures. Such impurities seem to be formed rather quickly even in the purest hydrocarbon if it is not protected from oxygen. Even if the complex is weak, concentrations of the same order of magnitude as the iodine concentration should be sufficient to keep iodine in solution, since equilibrium constants for reactions



are very high at liquid nitrogen temperature (Ref. 32 from C. van der Stolpe, Thesis, Amsterdam 1953). It is this complex formation which shifts the iodine absorption from 19.2 to about 22 kK on cooling to 77°K.<sup>33,\*\*</sup>

In order to produce spectral changes by photolysis at 77°K with light below 41 kK the iodine must be present in the complexed, "soluble" form; this was the case in the oxygen-containing hydrocarbons. These solutions showed at 77°K a peak around 39 kK, which is attributed to such a complex, although the donor has not been identified. Its rapid disappearance on photolysis is in accordance with what can be expected for a charge-transfer complex. The main results of this photolysis were new absorption bands at 25.5, around 28

\* During the work reported in Ref. 1 attempts were made to prepare solutions showing the triiodide bands without previous photolysis by cooling to 77°K a hydrocarbon mixture containing both HI and I<sub>2</sub>. Presumably due to the method of preparation — partial reduction of I<sub>2</sub> with H<sub>2</sub> — these solutions were free from polar oxygen containing molecules other than water, which obviously did not produce the triiodide bands. The nature of the 34.5 and 28.0 kK bands was thus questioned; however, they seem to be well established.

\*\* This explanation was not perceived in a preceding paper (Ref. 1). Therefore, the peak at 21.9 kK obtained on cooling a solution of I<sub>2</sub> and HI, was incorrectly attributed to a complex HI<sub>3</sub>, whereas in reality, it is a transition in the complexed iodine.

and at 34.5 kK. While the latter two were virtually unchanged by continued photolysis, the 25.5 kK peak increased for each additional photolysis period. These bands are identical with those arising in the photolysis of ethyl iodide in oxygen-containing hydrocarbons. Their nature, the disappearance of the 25.5 kK peak, and the subsequent growth of the triiodide bands have already been discussed in that section. A small peak with maximum at 13.7 kK, which in formation and disappearance followed the 25.5 kK peak, has not been identified.

When iodine in an oxygen-free hydrocarbon mixture was photolyzed at 77°K with light below 41 kK no spectral changes at all were observed.\* On the other hand, when frequencies up to 45.4 kK were used (this was achieved by photolyzing without glass filters, nickel sulfate solution being the cut-off filter), a definite change in the spectrum was found after warming to room temperature and recooling to 77°K — the typical alkene-iodine complex around 33 kK appeared. This complex was easily destroyed by photolysis at 77°K, yielding three clearly separated peaks at 43.0, 44.4, and 45.8 kK.

The reason for this difference is not understood at the present time. The higher photolysis energy in the second case should not be relevant, since hydrogen abstraction by iodine atoms, the most likely mechanism for the formation of alkene, does not require such a high activation energy. The difference could be that the precipitated iodine has no real absorption below 41 kK but merely scatters the light. The photolysis effects produced when frequencies up to 45.4 kK are used would then imply absorption in crystalline iodine between 41 and 45 kK. Although not a conclusive argument on this point it is interesting to note that, at room temperature, molecular iodine dissolved in oxygen-free hydrocarbons does absorb in this region, while it is transparent from 21—41 kK.

The possibility that the pure hydrocarbon can be photolyzed has been considered. That this is not the case was shown by photolyzing an oxygen-free hydrocarbon mixture at 77°K without glass filters for one hour. Iodine was added after warming the hydrocarbons to room temperature without opening the cell system. On recooling to 77°K no peak at 33 kK was found, and subsequent photolysis did not produce the described absorption around 44.4 kK.

The result of photolysis in an oxygen-free matrix is obviously the formation of alkene, since both the position, 33 kK, and the intensity,  $\epsilon = 14\,000\text{ M}^{-1}\text{cm}^{-1}$ , of the absorption maximum are typical for iodine-alkene charge-transfer complexes. Further, the three absorption bands at  $44.4 \pm 1.4$  kK arising from the complex on photolysis, agree very well with the absorption of 2-methylbutene-2 at 77°K described by Potts.<sup>27</sup> This is the type of alkene which would be expected when hydrogen is abstracted from the tertiary carbon atom in isopentane and 3-methylpentane. The correct assignment of the 44.4 kK bands was later given by Mulliken<sup>34</sup> as a transition between the ground state

---

\* This is analogous to the results reported for iodine in Ref. 1. Obviously the iodine precipitated in those experiments, which may have been due to the fact that the hydrocarbon solvents were used very soon after treatment with activated silica gel. From the negative photolysis results the conclusion was drawn that iodine atoms are not formed in the photolysis of iodine in a hydrocarbon matrix. As seen from the present work, this is true only in the special case that the iodine is precipitated and the highest photolysis frequency is 41 kK.

and the first excited triplet, supposedly a 3s state. The vibrational separation of the three bands by 1.4 kK agrees well with the C=C stretching frequency.

There is, however, a marked difference between the intensity of the triplet bands found by Potts and in the present work. If it is assumed that all alkene is present as complex at 77°K and that the complex is destroyed by photolysis resulting in free alkene, then the 44.4 kK peak has a molar extinction coefficient of about  $5000 \text{ M}^{-1}\text{cm}^{-1}$ , whereas Potts gives  $0.6 \text{ M}^{-1}\text{cm}^{-1}$ . It is possible that not all the alkene present was complexed and therefore the alkene concentration was higher than calculated from the intensity of the charge-transfer band. However, this is not very likely since the intensity ratio of the 33 kK and the 44.4 kK peaks is constant for different amounts of alkene-iodine complex (this is true even in the same experiment when the amount of alkene complex was successively increased by repeated photolysis with light above 41 kK). A probable explanation is the presence of the heavy iodine in this work, which increases the transition probability between states of different multiplicity. Even though the iodine concentration is as low as  $3 \times 10^{-5} \text{ M}$ , the enhancement of the singlet-triplet transition is not unreasonably large. Since the iodine is complexed by the alkene before the 44.4 kK triplet is formed, the distance between them should be small after photolysis, and therefore strong spin-orbit coupling can occur in the alkene. In accordance with this view is the fact that the triplet bands start to decrease when the matrix softens. It is interesting to note that the absorption around 44.4 kK is also present, though very weak, at room temperature in solutions which have been photolyzed without filters at 77°K long enough (about 2 h). The intensity in this case is only about one twentieth of that at low temperatures, which is as expected, since the iodine-alkene distance should be much larger.

With the interpretation of the band system around 44.4 kK given above the absence (or possibly very low intensity) of these bands before photolysis of the 33 kK peak is surprising. According to current charge-transfer theory this absorption, characteristic of free alkene at low temperatures, should be present as well as the charge-transfer absorption.

*Acknowledgements.* This investigation has been supported by *Air Force Office of Scientific Research*, OAR, through the European Office of Aerospace Research, United States Air Force, (in the beginning) and by *Malmfonden — Swedish Foundation for Scientific Research and Industrial Development*. A grant from the Faculty of Mathematics and Natural Sciences, University of Lund, is gratefully acknowledged.

#### REFERENCES

1. Timm, D. *Acta Chem. Scand.* **16** (1962) 1455.
2. Rand, S. J. and Strong, R. L. *J. Am. Chem. Soc.* **82** (1960) 5, and following papers by Strong *et al.*
3. Bridge, N. K. *J. Chem. Phys.* **32** (1960) 945.
4. Gover, T. A. and Porter, G. *Proc. Roy. Soc. (London)* **A 262** (1961) 476.
5. Nilsson, O. *Acta Chem. Scand.* *To be published.*
6. Potts, W. J. *J. Chem. Phys.* **20** (1952) 809.
7. Rosengren, K. *Acta Chem. Scand.* **16** (1962) 1421.
8. Rosengren, K., Sunner, S. and Timm, D. *Acta Chem. Scand.* **16** (1962) 495.
9. Rosengren, K., Sunner, S. and Timm, D. *Acta Chem. Scand.* **16** (1962) 467.



10. Vogel, A. I. *J. Chem. Soc.* **1943** 636.
11. Potts, W. J. *J. Chem. Phys.* **21** (1953) 191.
12. Norman, I. and Porter, G. *Proc. Roy. Soc. (London)* **A 230** (1955) 399.
13. Evans, D. F. *J. Chem. Phys.* **23** (1955) 1424.
14. Jones, T. O., Luebbe, R. H., Wilson, J. R. and Willard, J. E. *J. Phys. Chem.* **62** (1958) 9.
15. Herzberg, G. *Molecular Spectra and Molecular Structure I, Spectra of Diatomic Molecules*, 2nd Ed., van Nostrand, Princeton 1961.
16. West, W. and Schlessinger, L. *J. Am. Chem. Soc.* **60** (1938) 961.
17. Bunbury, D. L., Williams, R. R. and Hamill, W. H. *Ibid.* **78** (1956) 6228.
18. Bass, C. D. and Pimentel, G. C. *Ibid.* **83** (1961) 3754.
19. Luebbe, R. H. and Willard, J. E. *Ibid.* **81** (1959) 761.
20. Flournoy, J. M. and Judeikis, H. S. *VIIth Intern. Symp. on Free Radicals*, Cambridge 1963.
21. Cottrell, T. L. *The Strengths of Chemical Bonds*, 2nd Ed., Butterworths, London 1958.
22. Porret, D. and Goodeve, C. F. *Proc. Roy. Soc. (London)* **A 165** (1938) 31.
23. Steacie, E. W. R. *Atomic and Free Radical Reactions*, 2nd Ed., Reinhold, New York 1954.
24. Filseth, S. V. and Willard, J. E. *J. Am. Chem. Soc.* **84** (1962) 3806.
25. Kimura, K. and Nagakura, S. *Spectrochim. Acta* **17** (1961) 166.
26. Minnhagen, L. *Arkiv Fysik* **21** (1961) 415.
27. Potts, W. J. *J. Chem. Phys.* **23** (1955) 65.
28. Person, W. B. *J. Chem. Phys.* **38** (1963) 109.
29. Watanabe, K., Nakayama, T. and Mottl, J. *Final Report on Ionization Potential of Molecules by a Photoionization Method*, Department of Army Project No. 5B99-01-004, Ordnance R & D No. TB2-0001 OOR No. 1624 Contract No. DA-04-200-ORD 480 and 737, 1959.
30. Briegleb, G. *Elektronen-Donator-Acceptor-Komplexe*, Springer, Berlin 1961.
31. Kosower, E. M. *J. Am. Chem. Soc.* **80** (1958) 3261.
32. Ham, J. *J. Am. Chem. Soc.* **76** (1954) 3875.
33. Mulliken, R. S. *J. Am. Chem. Soc.* **74** (1952) 811.
34. Mulliken, R. S. *J. Chem. Phys.* **33** (1960) 1596.

Received May 5, 1966.