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Photolysis in Rigid Matrixes at Low Temperatures. An Intermediate of Photo-dehydrobromination

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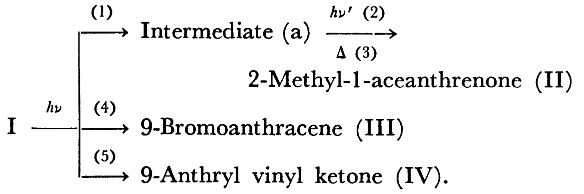
The intermediate of the photo-dehydrobromination of 9-(α-bromopropionyl)anthracene (I) to yield 9-anthryl vinyl ketone (IV) was detected by its electronic spectrum upon photolysis in polar solvent matrixes at 77 K. Approximately 80% of the initial photo-products is trapped as the intermediate. The remainder is observed as the final product IV formed directly from I. The intermediate is stable only below *ca.* 83 K in EPA. Above this temperature, it decomposes rapidly to form IV. No intermediate was detected for this reaction in the non-polar solvent matrixes at 77 K. Instead, a conformational change of IV with temperature was noticed. Based on the temperature and solvent effects on the stability of the intermediate, a loose structure where a hydrogen bromide is almost completely eliminated *via* a concerted mechanism is postulated for the intermediate. This is supported by the evidence that the main electrochemical reduction product of I is only 9-propionylanthracene. The temperature effects on the other photochemical reactions of I are also discussed in relation to the allowed molecular motions in rigid matrixes.

According to the previous results reported by the present author *et al.*,[1,2] the mechanisms of the intramolecular photochemical reactions of 9-(α-bromopropionyl)anthracene (I) can be summarized as follows:



The intermediate (a) to give II was rather stable and was readily detectable by its UV-absorption spectrum.[1,3]

The present detailed study of Reaction (5) in several matrixes at low temperatures has revealed that an intermediate to yield IV can also be detected spectroscopically at 77 K. Its stability is strongly dependent upon not only the temperature but also the nature of the matrix. Although no absorption due to the intermediate to give IV was detected in the non-polar solvent matrixes, an apparently different spectral change from that observed in the polar solvent matrixes was observed upon gradually softening the matrixes after the photolysis. This observation is explicable in terms of the presence of a second elementary process prior to giving IV, implying that Reaction (5) should involve at least one more transient state other than the newly found intermediate. These findings are of significance, since they will give us additional information as to the mechanism of the photo-dehydrohalogenation of α-haloketones.[4–6] A plausible structure of the intermediate will be given below, referring to the evidence demonstrated by the electrolysis of I.

Taken together with the previous results,[1–3] the present results also demonstrate that each of the Reactions (1) to (5) (revised (5), see below) shows a different temperature dependence. This appears to reflect a difference in the ease of the molecular motions which accompany each reaction mentioned above. Since the photochemistry of I involves rather a wide variety of molecular motions, it is expected that the present photochemical reactions will also provide the possibility of predicting what kind of molecular motion is allowed or prohibited in rigid matrixes upon photo-excitation.

Experimental

Materials. The preparation and purification of I have been described elsewhere.[1] Methylcyclohexane (MCH), isopentane (IP), ethanol (ET), diethyl ether, triethylamine (TEA), and 2-methyltetrahydrofuran (MTHF) were of a guaranteed grade from the Nakarai Chem. Co., Ltd. and were used after an ordinary distillation on a 30-cm Widmer column. Acetonitrile (ACN), a solvent used for the electrolysis of I, was repeatedly distilled over anhydrous aluminium chloride, sodium carbonate, and finally calcium hydride according to the method of Walter and Ramaley.[7] Dry tetrabutylammonium perchlorate (TBAP) or potassium perchlorate was used as a supporting electrolyte (*ca.* 0.1 M).

Procedures. The electonic absorption spectra at the controlled low temperatures were recorded in the same way as has previously been described.[8] For photolysis at low temperatures, a glass gas-inlet pipe at the bottom of a transparent Pyrex Dewar vessel, in which a reaction cell was set, was attached directly to the inlet of a metal Dewar vessel which served as a liquid-nitrogen reservoir. From the bottom of the Pyrex Dewar vessel, boiled cold nitrogen gas was admitted by means of a power resister in order to control the temperature in the range of 90—200 K. After the thermal equilibrium had been attained, the temperature was measured with a copper-constantan thermocouple which was directly immersed in the reaction cell. Photolysis at 77 K was performed by immersing the reaction cell directly in a transparent Pyrex Dewar vessel containing liquid nitrogen. The reaction cells were made of quartz and were 1.0 and 0.2 cm in path length. When the matrixes were unstable toward temperature variation, the cells of the smaller path length were employed. The irradiation source was an Ushio 100 W medium-pressure mercury-arc lamp. A Pyrex Dewar vessel or a water-cooled jacket made of Pyrex glass served as a glass cut-off filter. Since the photolysis of I is essentially independent of whether or not the solution is deaerated, the sample solutions were not degassed unless otherwise stated.

A conventional H-shaped electrolysis cell, the center of which was separated into two compartments by means of a sintered glass-plate, was employed to electrolyze I at a constant potential. Working and auxiliary electrodes were platinum plates of 2×2 cm. A reference-electrode (silver wire) compartment was isolated from the solution to be electrolyzed by means of a glass frit. The solutions were deaerated by bubbling dry nitrogen gas through. To control the potential, a Hokuto Denko Model HA 101 potentiostat and a Hewlett Packard Model 3300 A function generator were used. Electrolysis products were analyzed by column chromatography on silica gel with benzene after removing the solvent and were identified by comparison (IR- and UV-absorption spectra) with the authentic samples.

For the studies of the cyclic voltammograms of I under a thoroughly degassed and dried condition, a cell similar to that which had previously been prepared for ECL observation was used.[9)]

Results

Photolysis at Low Temperatures. Figure 1 shows the absorption spectra of I before and after photolysis in EPA (diethyl ether, isopentane, and ethanol, 5 : 5 : 2 by volume) at 77 K. All the spectra were taken at 77 K. As is shown in Fig. 1b, the absorption of I disappears with irradiation and, instead, we obtain the red-shifted broad band superposed upon by the sharp band with peaks at 364 and 384 nm. The absorbances of these broad and sharp bands increase only with irradiation and, after the thorough consumption of the reactant (spectrum (b)), continued irradiation causes no further spectral change at 77 K. Upon warming the matrix, however, the broad band disappears and changes into a sharp spectrum with the 0-0 band at 384 nm (spectrum (c)). Since IV is the sole photolysis product in EPA at 77 K, as has previously been verified,[1,2)] the (c) spectrum is solely due to IV.

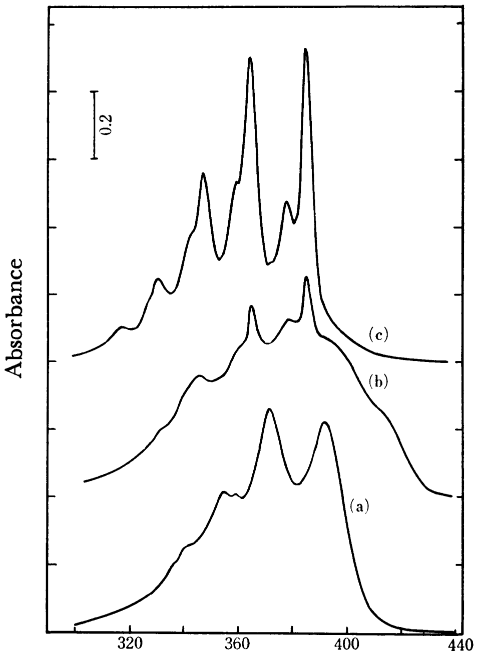


Fig. 1. Photolysis of I (7.1×10^{-5} M) in EPA at 77 K. (a) Before irradiation, (b) after irradiation for 3 h, (c) the spectrum observed at 77 K immediately after warming the sample with the (b) spectrum to room temperature. The (c) spectrum is due to IV. For the sake of clarity, the base line (right-hand side) of each spectrum is shifted by an appropriate amount of absorbance in Figs. 1, 3, 4, and 5.

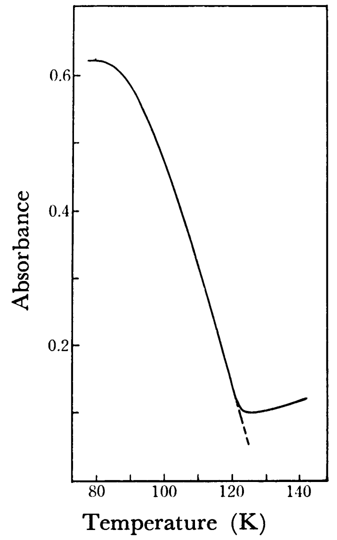


Fig. 2. Change in the absorbance (at 395 nm) of the intermediate with temperature.
A rise in the absorbance at around 123 K is caused by the opacity of the matrix on softening. This figure shows that the intermediate is stable only below 82—83 K. Temperature-rise time: *ca.* 4 min (77—83 K); *ca.* 5 min (83—123 K).

Therefore, the broad band on the longer-wavelength side can reasonably be attributed to an intermediate (hereafter called intermediate (b)) to give IV.

Figure 2 shows how labile the intermediate (b) is against a rise in the temperature. The change in the absorbance of the intermediate formed in EPA was monitored at 395 nm against the temperature by allowing the matrix to grow warmer, and was displayed on an X-Y recorder. From this curve it is apparent that the intermediate (b) is stable only below 82—83 K. In fact, no absorption due to the intermediate (b) was observed during the photolysis of I in EPA at 93 K. At 77 K, however, the intermediate was very stable and no absorption change was observed after allowing the photolyzed solution to stand in the dark at 77 K for several hours. A similar phenomenon was also observed in other transparent-matrix-forming polar (or slightly polar) solvents such as MTHF, ET, and TEA.

The presence of the small sharp peaks before warming the matrix, as is shown in Fig. 1b, implies that a part of the photoeliminated hydrogen bromide molecules can escape from the solvent cage, probably because of excess excitation energy, and that IV is formed directly from I. The percentage of this escape is calculated to be *ca.* 20%[10)] in EPA and does not differ significantly in MTHF, ET, TEA, and in EPA.

In contrast, in a non-polar and rather soft MCHIP matrix (methylcyclohexane and isopentane, 3:1 by volume),[11)] no absorption similar to that which was observed in EPA was detected, in spite of almost a 100% yield of IV.[2)] The results of the spectral change upon photolysis are shown in Fig. 3. The (c) spectrum was obtained at 77 K once after warming the photolyzed solution with the (b) spectrum to room temperature. Although the absorption due to the in-

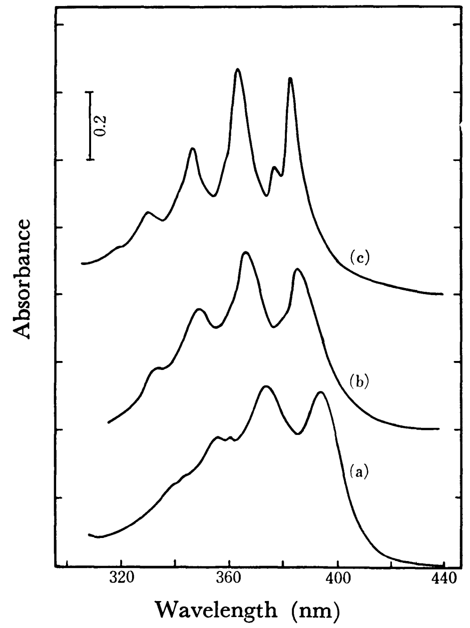


Fig. 3. Photolysis of I (5.3×10^{-5} M) in MCHIP at 77 K. (a) Before irradiation, (b) after irradiation for 3 h, (c) the spectrum observed at 77 K immediately after warming the sample with the (b) spectrum to room temperature. The (c) spectrum is due to IV. No absorption due to the intermediate (b) is observable.[11,13]

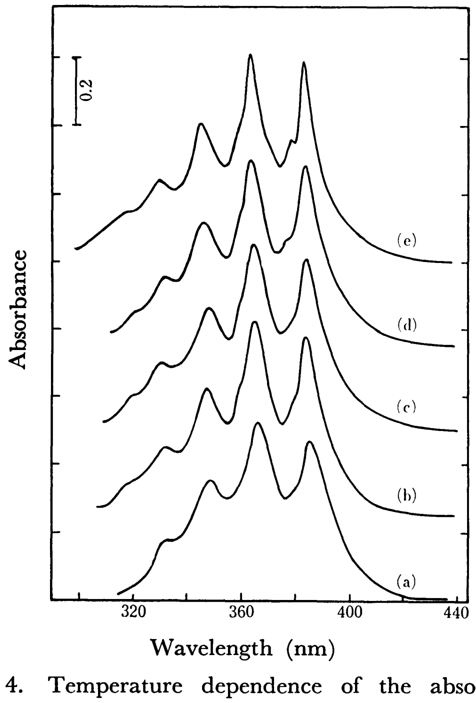


Fig. 4. Temperature dependence of the absorption spectrum of the photo-product formed in MCHIP at 77 K.
(a) 77 K, (b) 98 K, (c) 114 K, (d) 127 K, (e) 144 K. The (e) spectrum apparently differs in the sharpness of the bands from the other spectra.

termediate (b) cannot be observed in MCHIP, the absorption spectra of the photolyzed solution apparently differ between before and after softening the matrix.

Figure 4 shows at what temperature this spectral change occurs. After thorough photolysis in MCHIP at 77 K, the absorption spectra were recorded upon warming the matrix to several constant temperatures. In the neighborhood of 140 K, a rather broad band is seen to change into a sharp band with a greater molar extinction coefficient. Since the medium at these temperatures is fluid enough to allow free molecular motions,[12] the observed spectral change cannot be explained in terms of a change in the rigidity of the matrix with temperature. A possible cause of this spectral change will be discussed later,[13] in relation to a conformational change in IV.

A similar spectral change was also detected during

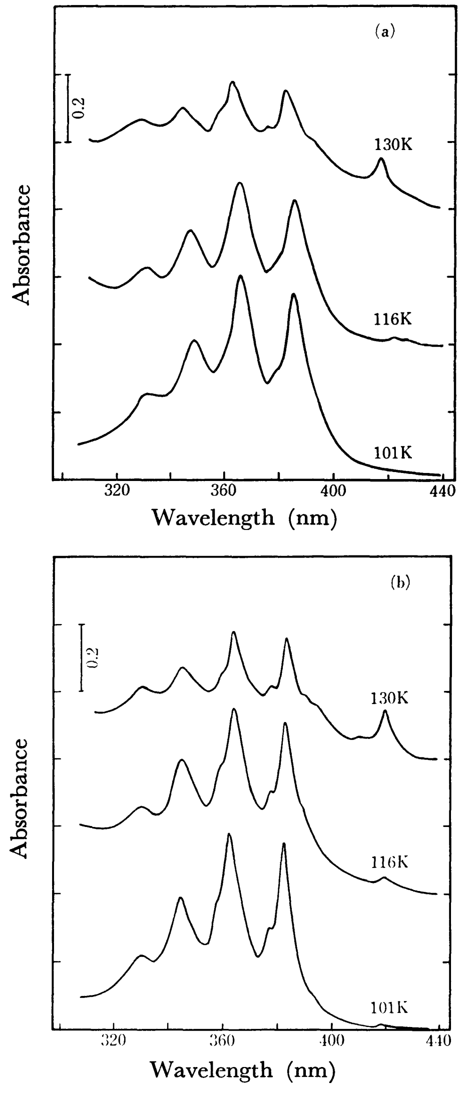


Fig. 5. Absorption spectra of the photo-products of I formed at several low tempratures.
(a) Immediately after photolysis;
(b) after warming to room temperature.
The samples were photolyzed at the indicated temperatures and their spectra were observed at 77 K (Fig. 5a) and were then warmed once to room temperature before the second observation at 77 K (Fig. 5b). All the spectra in Fig. 5b are sharper in shape than the corresponding spectra in Fig. 5a. The small peaks at 418 nm are due to II.[2,8]

the photolysis of I in MCHIP at temperatures higher than 77 K. The results are shown in Fig.5. Comparing Fig.5a with 5b, a difference in the sharpness of the bands can be seen particularly at 383 nm.

In the first instance, a radical species derived from the homolysis of the C–Br bond may be considered as an appropriate candidate for the intermediate (b). However, no ESR signal was observed upon photolysis at 77 K in either polar- or non-polar-solvent matrixes. Thus, Reaction (5) does not appear to involve a radical mechanism but to proceed *via* a concerted elimination mechanism.[6)]

In order to confirm this from a different point of view, the electrolysis of I was carried out.

Electrolysis. The cyclic voltammograms of I before and after electrolysis at a constant potential are shown in Fig. 6. A similar result was obtained under a thoroughly degassed and dried condition.

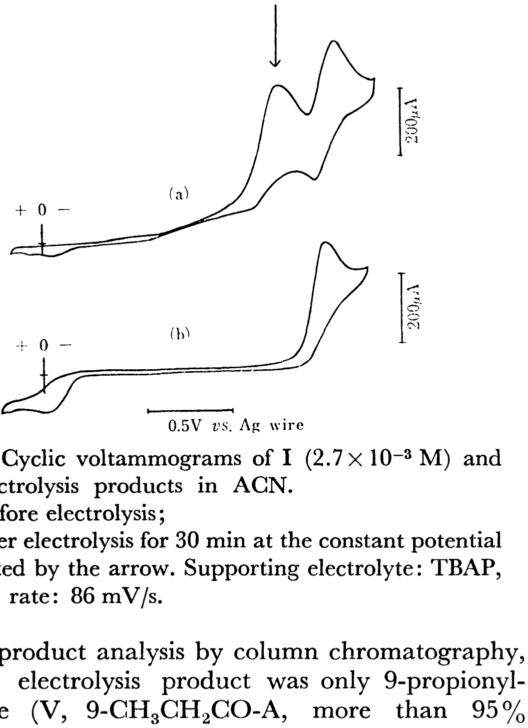


Fig. 6. Cyclic voltammograms of I (2.7×10^{-3} M) and its electrolysis products in ACN.
(a) Before electrolysis;
(b) after electrolysis for 30 min at the constant potential indicated by the arrow. Supporting electrolyte: TBAP, Sweep rate: 86 mV/s.

Based on product analysis by column chromatography, the main electrolysis product was only 9-propionylanthracene (V, 9-CH_3CH_2CO-A, more than 95% of the detected products), a product of bromine atom replacement. Thus, the first and second peaks in Fig.6a correspond to the reduction-wave peaks of I and V respectively.[14)] The fact that the loss of a bromide ion from the $[I]^{\cdot-}$ anion radical is rapid is demonstrated by the absence of an anodic wave of the reoxidation of $[I]^{\cdot-}$. This is the case even at low temperatures where the anion radical might be stabilized.[16)] Similar results were obtained with both TBAP and potassium perchlorate, the latter of which has no hydrogen atom to donate.

Referring to the previously reported reduction reaction mechanism of organic halides,[17)] the present result may be interpreted by the following mechanism;

$$\mathrm{I} + e \longrightarrow [\mathrm{I}]^{\cdot-} \longrightarrow 9\text{-}CH_3\dot{C}HCO\text{-}A + Br^-,$$

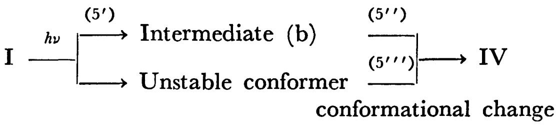
$$9\text{-}CH_3\dot{C}HCO\text{-}A \xrightarrow{\text{solvent}} \mathrm{V},$$

$$\mathrm{V} + e \longrightarrow [\mathrm{V}]^{\cdot-} \longrightarrow \text{rapid follow-up reactions.}^{15)}$$

A 9-$CH_3\dot{C}HCO$-A radical, formed as a result of bromide ion elimination, immediately abstracts a hydrogen atom from the solvent to give V,[18)] but not IV. Thus, the intermediacy of the ketonyl radical in the photolysis of I may reasonably be ruled out. In considering the detailed mechanism of Reaction (5), it is noteworthy that none of the main photolysis products[1)] was found in the electrolysis products; the photochemistry of I in ACN is essentially the same as that in ET or in MCH.

Discussion

A Postulated Structure of the Intermediate (*b*). Summarizing the above-mentioned facts, Reaction (5) may be rewritten as follows:



Each process, of course, depends on the nature of the matrix.

We must now consider the structure of the intermediate (b) and the origin of the conformational change indicated in the above scheme. Based on the facts that no ESR signal was detected and that the main electrolysis product was solely V, a radical species such as 9-$CH_3\dot{C}HCO$-A can safely be excluded as an appropriate intermediate to give IV. Taking into account the fact that the intermediate is very labile toward a rise in the temperature from 77 K, completely unstable in soft matrixes, and gives a single product IV upon sofetening the matrix, a structure in which dehydrobromination has almost been completed appears to be most appropriate as a structure of the intermediate (b). A postulated structure is dipicted in Fig. 7a. The dotted-line bonds will be much weaker than the broken-line bonds. This structure is reminiscent of the structure frequently referred to as the four-membered *syn*-elimination transition state in the pyrolytic dehydrohalogenation reactions of organic halides.[6,20)] Its loose structure could explain the broad absorption spectrum of the intermediate. Although the intermediacy of a tight radical pair formed as a result of homolysis of the C–Br bond may not be ruled

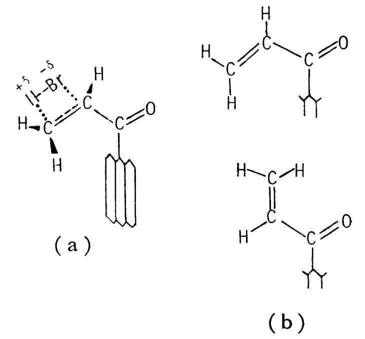


Fig. 7. A plausible conformation of the intermediate (b) (Fig. (a)) and two conformers of IV (Fig. (b)). It is not obvious which conformer is more stable.

out completely, we may expect, in such a case, the formation of V in an appreciable amount.[21] To the author's knowledge, this is the first case where an intermediate of photo-dehydrohalogenation has been detected by its electronic absorption spectrum.

Figure 7b shows two possible conformers of IV. Acrylaldehyde serves as the simplest model compound for the substituent of IV and *s-trans*-acrylaldehyde is reported to be more stable than *s-cis*-acrylaldehyde.[22] Thus, the conformational change in the substituent of IV from *cis* to *trans* or *vice versa* may give rise to the observed spectral change at around 140 K, where the potential barrier of the conformational change will come to be surmounted. The reason for the absence of a similar change in EPA or in MTHF may be that interactions between I or IV and solvent molecules (hydrogen-bonding, *etc.*)[23] can preferentially stabilize one of the conformers.

Allowed Molecular Motions in the Rigid Matrixes. It is very important and instructive to know what kinds of molecular motions are allowed in rigid matrixes, particularly upon photo-excitation. However, there are few such related works, except for detailed studies of *cis-trans* photoisomerization at low temperatures.[24] Fortunately, the present results provide the possibility of investigating a wide variety of allowed molecular motions in matrixes by observing the temperatures at which the photochemical and follow-up dark reactions of I are prohibited. The sequence of the prohibition of the present reactions is as follows, in increasing order:

$$(5') \ (77\text{ K}) < (2) \ (77\text{ K, very slow}) < (5'') \ (85\text{ K}) <$$
$$(4)^{1)} < (1) \ (100\text{ K}) < (5''') \ (140\text{ K}) < (3)^{1)}$$

In parentheses are given the approximate lowest temperatures where the indicated reactions can still be observed. The first inequality means that the photodehydrobromination from the intermediate (a) is very slow, though detected at 77 K, as compared with Reaction (5′).[25] Reactions (3), (5″), and (5‴) are thermal reactions, the last of which is observed in MCHIP. From the above sequence, it can be said that:

i) The elimination of small molecules (*e.g.*, HX, N_2, CO_2) which is not accompanied by a large structural change will occur readily even at 77 K.[26,27] In the hard matrixes, however, the eliminated molecules cannot be expelled out of the solvent cage, but stay very near to the parent pieces; in a fortunate case, the intermediate(s) will be detected.

ii) A large rotational motion of a group equal to or greater than an acetyl (or propionyl) group is strongly prohibited at 77 K.[2]

iii) Compared with photochemical reactions, the corresponding thermal reactions (*i.e.*, the reaction to yield the same product(s)) are generally retarded much faster upon cooling, as is demonstrated by a comparison of Reactions (2) and (3).[1] This does not mean that the local heating due to irradiation may be of some help to the photolysis of I in the frozen matrixes.

Even for photochemical reactions, some amount of activation energy is necessary, and hence the prohibition of photochemical reactions in frozen matrixes does not always mean the prohibition of the necessary molecular motion due to the matrix rigidity. Hence, if a photolytic reaction which belongs to item i) cannot be detected in frozen matrixes, the activation energy of that reaction may be said to play a dominant role in the prohibition. On the basis of the temperature effect on its reaction, every photochemical reaction reported herewith seems principally rigidity-controlled and Reactions (3) and (5‴) are activation-energy controlled.

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10) Prolonged irradiation at 77 K did not cause an increase in this percentage, implying that under the present conditions, the temperature rise due to local heating did not exceed 6—7 K.

11) In either MCH or IP, no intermediate was detected upon the photolysis of I at 77 K. In the softer matrixes composed of the higher ratio of IP to MCH (*e.g.*, IP and MCH 3 : 1 or 10 : 1 by volume), the absence of the intermediate (b) can more clearly be demonstrated than is shown in Figs. 3 and 4, since the photolyzed solutions give slightly sharper absorption bands at 77 K before warming.

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18) Another reaction mechanism, $9\text{-}CH_3\dot{C}HCO\text{-}A+e\rightarrow$ $[9\text{-}CH_3\ddot{C}HCO\text{-}A]^- \xrightarrow{[H^+]} V$, may partly participate in giving V.[19] The controlled-potential coulometry of I, however, showed that the number of electrons needed to give V was close to one (0.98).

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