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Photochemistry of "Salted" Quadricyclane and Norbornadiene: Alkali Halide Color Centers as Catalysts

Ewa S. Kirkor, Vincent M. Maloney, and Josef Michl*

Contribution from the Center for Structure and Reactivity, Department of Chemistry, The University of Texas at Austin, Austin, Texas 78712-1167. *Received June 3, 1988*

Abstract: Quadricyclane "salted" in CsI or KBr or otherwise in contact with these solids is rapidly converted into norbornadiene under conditions that induce color center formation in the alkali halide: rapid-growth vapor deposition, or UV or X-ray irradiation. The reaction proceeds only at temperatures where the H centers are mobile. At lower temperatures, UV irradiation of norbornadiene converts it into quadricyclane in the usual fashion.

The unusual ionic environment to which nonpolar organic compounds "salted" in alkali halides[1] (i.e., "preserved" by incorporation in a salt) are exposed may be expected to affect their reactivity. We now report an investigation of the classical photochemical system[2-5] norbornadiene (**1**)–quadricyclane (**2**) in CsI and KBr matrices, using salting deposition conditions known[6] to yield single-molecule isolation in these matrices for another nonpolar dopant, $Fe(CO)_5$.

We find strong evidence for the involvement of alkali halide color centers of the "missing electron" type (H center) in the chemistry of the organic dopants. The critical part of the structure of this center is believed to be best approximated as $(I-I)^{\bullet-}$ associated with two positive counterions. Its negative counterpart, the F center, is formally obtained by replacing a halide anion in the lattice by a trapped electron. At temperatures above ~90 K, the electron deficiency moves easily through CsI lattice by the chain "substitution" process $(I-I)^{\bullet-} + I^- \rightarrow I^- + (I-I)^{\bullet-}$, which requires minimal atomic displacements.[7]

In fluid solutions in ordinary organic solvents, irradiation of **1** at 254 nm produces photochemically stable **2**,[2,3] which has negligible absorption at this wavelength. Upon triplet sensitization, the valence isomers **1** and **2** are interconverted. The resulting composition of the photostationary state is governed not only by triplet energy of the sensitizer but also by its ability to form transient complexes with the substrates.[8]

The isomerization of **2** to **1** can be accomplished by heating,[2] and the gas-phase activation energy for the thermal reaction is 38 kcal/mol.[9] The transformation also occurs at room temperature in homogeneous solutions containing one-electron oxidants. This process follows a reversible electron-transfer pathway with spontaneous isomerization of the radical cation $\mathbf{2}^{\bullet+}$ to $\mathbf{1}^{\bullet+}$.[10-21] Irradiated semiconductors such as CdS, ZnO, and TiO_2 also catalyze the isomerization of **2** to **1**.[22,23] The oxidation potentials of both molecules (**1**, 1.54 V; **2**, 0.91 V against SCE[16]) are lower than the energies of the semiconductor valence-band holes (CdS, 1.6 V;[24] ZnO, 2.4 V;[24] TiO_2, 2.3 V[25] against SCE). A hole that diffuses to the semiconductor surface oxidizes **1** and **2** to their corresponding radical cations, $\mathbf{1}^{\bullet+}$ and $\mathbf{2}^{\bullet+}$. The radical cation $\mathbf{2}^{\bullet+}$ isomerizes readily into $\mathbf{1}^{\bullet+}$,[15] which is subsequently reduced to **1**. The overall efficiency of the process is low.[22]

Experimental Section

Materials. Quadricyclane, norbornadiene, and iron pentacarbonyl from Aldrich Chemical Co. and CsI, KBr, and NaCl (99.998% purity) from AESAR Co. were used as received.

Equipment. Depositions of **1** or **2** into CsI or KBr were done either in a home-made UHV deposition apparatus or in an Air Products Co. Displex 202 cryostat as described in detail elsewhere.[6] The cryostat was used for all low-temperature measurements (≥10 K). Some room- and all higher temperature measurements as well as all X-ray irradiations were performed in a 2-in. stainless steel vacuum chamber equipped with either CsI or quartz windows, evacuation ports, sample holder, heater, and thermocouple.

For irradiations we used a low-pressure mercury lamp (254 nm), a 1000-W high-pressure xenon lamp with a PTI SN 86-161 monochromator, or the 308-nm line of an XeCl excimer laser (Lumonics HyperEX 400). The IR spectra were measured with 1-cm^{-1} resolution on Bomem DA3.02, Nicolet SX-20, or Nicolet SX-60 instruments and 4-cm^{-1} resolution on Digilab FTS 40. A Phillips MGCO+ source with an MCN101 tube and a tungsten target (60 krad/h, 80 kV, 25 kW) was used for X-ray irradiations. Products of solution irradiations were analyzed by gas chromatography by using a Varian 3300 instrument with a 20-m DBI column from J&W Scientific (1-μm film thickness) or a 5995-HP GC–MS instrument with a 20-m HP-1 column (5-μm film thickness). UV spectra were measured on a Cary 2300 (Varian) spectrometer with 1-nm resolution between 200 and 900 nm.

Procedures. The deposition conditions were those established[6] for single-molecule isolation of iron pentacarbonyl in CsI and KBr matrices. The matrix ratio was kept below 1:400 by depositing the salt at the previously optimized rate[6] and allowing **1** or **2** to evaporate from a reservoir kept at temperatures from −75 to −40 °C. The samples prepared in the cryostat were used directly after deposition.

The deposition times for UV measurements were short (~30 min), thus limiting the amount of unwanted condensates. In spite of a decrease of transmittance due to evaporation of excess volatiles, thin samples preserved reasonable optical quality up to room temperature.

The samples prepared in the UHV apparatus were freed from merely adsorbed dopant by evacuation at 10^{-9} Torr at room temperature for at least 3 h and transferred in a drybox to a sample cell. Some of the

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quadricyclane and the cocondensed background gases evaporate from the cryostat deposits while the temperature is being raised.

The dopants were identified by their distinctive IR bands in low-temperature spectra. Although at 298 K the observed peaks were often weak and on a high background, the major features were reproducible. Characteristic bands for **1**[26,27] were observed at 1312, 728, and often, 658 cm^{-1}, and for **2**[28] at 1237 and 765 cm^{-1}.

An attempt to measure the kinetics of the thermal isomerization of **2** to **1** failed. No isomerization occurred below 350 K and at higher temperatures neither **2** nor **1** could be detected, presumably due to diffusion and evaporation from the matrix sample.

Considerable attention was paid to the exclusion of all traces of water from the samples. We have discarded data from all experiments in which evidence for the presence of water was obtained either from its IR absorptions or from the presence of U_2 centers in the UV absorption.[29-31]

Results

Matrix Deposition. While codeposition of **1** with CsI or KBr followed by a warm-up to room temperature produces the expected salted **1**, a similar deposition of **2** produces a mixture of **1** and **2** in the salt matrix. Qualitatively similar **1** to **2** ratios were found in experiments with CsI and with KBr. Low-temperature IR spectra demonstrate that only **2** is present at 20 K immediately after deposition and that the partial conversion to **1** occurs in the dark between 90 and 130 K.

The appearance of both **1** and **2** in salt deposits where **2** was the only dopant is therefore not due to trivial reasons such as thermal conversion of **2** to **1** due to radiative heating, contact of vapors with the hot salt oven, or the release of heat of condensation as the salt is codeposited with the dopant. No thermal decomposition was observed in depositions of the thermally much more fragile $Fe(CO)_5$ under similar conditions.[1,6]

The UV–visible spectra of doped and undoped CsI matrices, as initially deposited, reveal weak absorbances characteristic of H and F color centers. They are stable below 15 K and grow significantly upon irradiation with a low-pressure mercury lamp.

We associate the initially generated H center with a peak at 365–372 nm. In an undoped single crystal of CsI at 80 K this center absorbs at 400 nm.[32] In other alkali iodides it appears from 380[33] to 404 nm.[34] In CsI doped with Na^+ or Tl^+ it is observed at 410 nm.[35] In argon matrix isolation at 10 K, $Cs^+I_2^{\bullet -}$ absorbs at 366 nm.[36]

We associate the F center with a broad band at 736 nm, a position identical with that observed in single crystals of CsI.[37]

A warm-up of an irradiated CsI matrix that is either undoped or doped with **1** causes several transformations of the color centers, presumably analogous to those that have been studied in other alkali halides[38,39] and believed to be associated with defect formation and with changes in the geometrical arrangement of nearby F and H centers. In particular, the maximum of the 365-nm peak of the H center shifts to 372 nm upon prolonged irradiation, and subsequently to longer wavelengths upon annealing, reaching approximately 380 nm at 40 K. The same shift has been reported for $Cs^+I_2^{\bullet -}$ in an annealed argon matrix.[36] At 135 K the maximum reaches 415 nm. No further shift but only a gradual intensity loss occurs when the temperature is increased further. In our samples the 348–355-nm maximum associated with $I_3^{\bullet -}$[40] appears at ~70 K, is fully developed at ~135 K, and decays above 150 K. The F centers decay at 40–135 K. Above 210 K, the last H centers disappear.

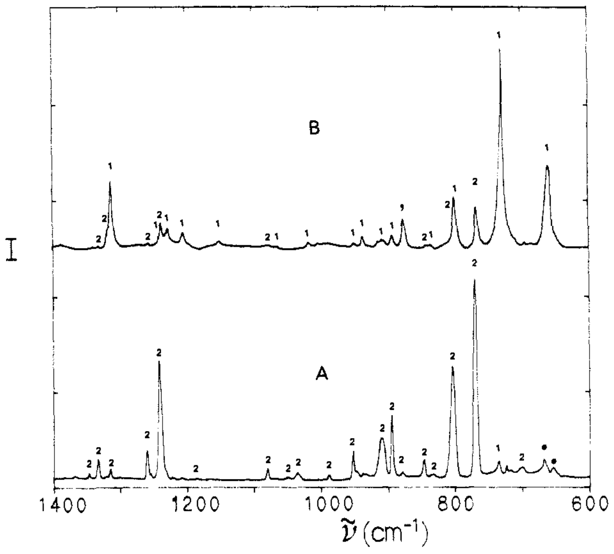

Figure 1. FT-IR absorption of **2** salted in CsI, arbitrary scale. A: 15 K, before irradiation. B: After warm-up to 130 K and 10-min irradiation at 254 nm. The peaks are labeled as belonging to **1** or **2**.

In a matrix doped with **2** the decay of F and H centers is already completed between 70 and 85 K and the $I_3^{\bullet -}$ absorption never develops.

Photochemistry: Matrix. Irradiation of salted **1** with a low-pressure Hg lamp at temperatures below 90 K in CsI and 290 K in KBr converts it to **2**, as judged by the FT-IR spectrum. At higher temperatures, no photoconversion takes place.

Irradiation of salted **2** with the same lamp or with a 308-nm laser beam at temperatures below 90 K in CsI and below 290 K in KBr has no effect. Above these temperatures, the irradiation causes an isomerization of **2** to **1** (Figure 1).

A gradual slow decrease in the overall intensity of the IR spectra of **1** or **2** is observed upon extended photolysis in a CsI matrix above 90 K. Below 90 K, this gradual photodestruction does not seem to occur.

Since the ultrahigh-vacuum apparatus was being used for the experiments with **1** and **2** described here in the same period of time as for the experiments with $Fe(CO)_5$ described in ref 6, we have also performed a control experiment in which a matrix doped with **2** was intentionally doped with $Fe(CO)_5$ as well. This changed the observed photochemical behavior of **2** dramatically. Irradiation of a CsI matrix containing $Fe(CO)_5$ and **2** (480:1:1) at 250, 300, or 350 nm causes no isomerization to **1** at any temperature in the 10–298 K range. This was true even after 4 days of irradiation, when all $Fe(CO)_5$ had been destroyed and the matrix was transparent in the UV down to 240 nm.

Radiolysis. A 1-h X-ray irradiation of **2** salted in KBr at room temperature converts it to **1**. An equally long X-ray irradiation of neat liquid **2** degassed by four freeze–pump–thaw cycles results in no detectable reaction.

Photochemistry: Solution in Contact with an Alkali Halide Surface. Complete photoisomerization of **2** to **1** occurs upon irradiation with monochromatic 250–350-nm light within hours in CsI pellets and between previously irradiated CsI plates containing traces of color centers. Solid KBr has a much smaller effect, and solid NaCl does not affect the photoreactivity of **1** or **2**. Similar irradiation of **2** dissolved in a methanol solution of CsI or KBr has no effect.

Irradiation of a 1×10^{-2} M solution of **2** in pentane containing a stirred suspension of powdered CsI crystals with a low-pressure

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Hg lamp leads to a complete conversion to **1**. No dark reaction occurs under otherwise identical conditions. The presence of a copper wire coil in the unirradiated portion of the stirred reaction vessel does not slow down the conversion of **2** to **1**. When CsI is replaced by KBr in these experiments, no photochemical reaction occurs.

Discussion

The spontaneous transformation of salted **2** into **1** in the dark as the initially deposited doped CsI matrix is warmed to 90–130 K, or the KBr matrix to 290 K, demonstrates that the cold alkali halide deposits are capable of storing energy and using it for a chemical transformation at a higher temperature.

It seems clear that the metastable energy is stored in the form of color centers.[41] These are known to be generated both upon quick condensation[42,43] and upon UV irradiation[44] of alkali halides. We observe them in our UV–visible spectra immediately after deposition and in much larger amounts after subsequent UV irradiation. The relatively low thermal stability of the color centers produced by quick vapor deposition, relative to color centers in single crystals, is undoubtedly due to a high defect concentration, known[45,46] to accelerate the decay of color centers in alkali halide crystals.

Both the low-pressure mercury lamp and the 308-nm laser used in the present investigation are capable of inducing F and H color center formation efficiently in CsI and with a low quantum yield in KBr,[44] but not in NaCl.[44]

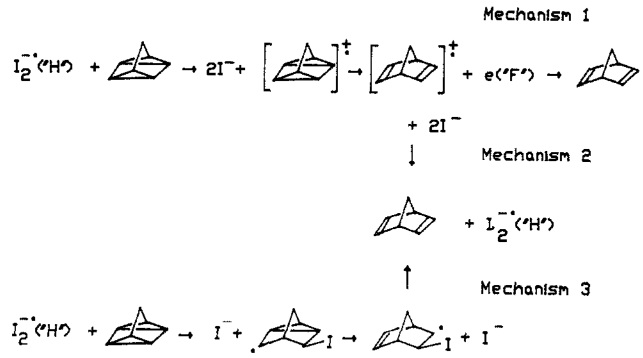
A mechanism by which the energy stored in the color centers is used to effect the transformation of **2** to **1** is suggested by the analogy to the known solution radical-cation mechanism of isomerization,[10-18,20,21] and particularly to that induced by a hole in the valence band of a semiconductor.[21,22] We believe that the active agent for the **2** → **1** transformation observed in our experiments is the H center. As long as this is immobile, it remains inactive, but at temperatures where it diffuses through the solid it becomes effective. This proposal is supported by the coincidence of the onset of isomerization of **2** to **1** (90 K) with the maximum of thermoluminescence observed upon the warmup of a pure CsI condensate (86 K). This emission has been assigned to the hopping of the H centers and their recombination with the F centers.[7,47] In our samples, the recombination of H and F centers occurs concurrently with the catalyzed **2** → **1** transformation and eventually depletes the supply of the catalyst.

Thus, we propose that our photochemical results can be accounted for by invoking an H-center catalyzed **2** → **1** conversion in the temperature range where these centers are mobile and ordinary **1** → **2** photoconversion[5,19] at temperatures where they are not.

Two mechanisms involving electron transfer and one that does not can be thought of readily as plausible candidates for the catalytic action of the H center (Scheme I). In both electron-transfer mechanisms, the reaction proceeds by electron transfer from **2** to the H center. This can be represented chemically as the formation of 2I^- and $\mathbf{2}^{\bullet+}$ from $\mathrm{I}_2^{\bullet-}$ and **2**. There is some precedent for the trapping of color centers by neutral molecular species. Adsorption of NO on a rapidly condensed film of alkali halides results in color center decay and the production of NO^+ and NO^- ions.[43] Adsorption of water, chlorine, or hydrogen chloride was also found to assist the decay of color centers.[48]

In the second step, the radical cation $\mathbf{2}^{\bullet+}$ isomerizes to $\mathbf{1}^{\bullet+}$ in the known fashion.[10-18,20] Next, electron transfer from a donor yields **1**. The exact nature of the electron source that converts $\mathbf{1}^{\bullet+}$ to neutral **1** distinguishes the first two mechanisms (Scheme I):

Scheme I. Possible Reaction Mechanisms for the Phototransformation of Salted **2** into **1**



(i) It could be an F center, in which case each isomerization event would correspond to a mutual annihilation of an H and an F center. Under conditions of irradiation, constant generation of holes and promotion of electrons to the conduction band offers a ready supply of H and F centers, which can use the dopant as a recombination center. However, this mechanism probably cannot be solely responsible for the observations. It has difficulty accounting for the **2** → **1** isomerization in the warmup phase of the experiment after **2** was first deposited, as the F centers are normally not very mobile in the dark at 90–130 K.

(ii) In a second and perhaps more likely mechanism, the donor is the interstitial I^- ion produced when the H center was first neutralized. Transfer from this donor to $\mathbf{1}^{\bullet+}$ regenerates the H center, which is thus acting as a true catalyst. The direction of the initial electron jump from **2** to H and the direction of the subsequent electron jump from I^- to $\mathbf{1}^{\bullet+}$ are plausible in view of the much higher oxidation potential of **1** (1.54 V) than **2** (0.91 V). This second mechanism can operate even if only the H centers are mobile and is thus capable of accounting for the isomerization during the initial dark warm-up period.

(iii) A third mechanism by which an H center could convert **2** to **1** avoids the radical-cation stage altogether. It assumes that the H center acts as a source of an iodine atom, which makes a covalent bond to a carbon in **2** to yield an intermediate radical of the cyclopropylmethyl type. This isomerizes and subsequently loses an iodine atom again, regenerating the H center. This mechanism also uses H centers as true catalysts and accounts for the isomerization occurring during the initial dark warm-up period.

We have no basis for deciding between the second and the third mechanism from our matrix experiments.

The catalysis of the solution transformation of **2** to **1** by irradiation of a stirred suspension of powdered CsI, but not KBr or NaCl, can be understood in terms of the same mechanisms. Now, only the H centers that are formed at the surface or diffuse to it are effective as catalysts. The charge-transfer mechanism ii then becomes identical with that accepted as the basis of the photocatalytic action of semiconductors such as CdS,[24,25] ZnO,[24,25] or TiO_2.[25] The absence of any observable discoloration and the fact that the presence of a copper wire in the dark portion of the vigorously stirred solution had no effect on the reaction rate suggests that no significant buildup of free iodine occurs in the solution. This is in itself insufficient to exclude mechanism iii since iodine atoms would be scavenged very efficiently by **1** and **2**. The reason why CsI powder is active while KBr and NaCl powders are not is undoubtedly related to their optical properties. The 254-nm light is not absorbed efficiently by the latter two materials, particularly NaCl, and no color centers are formed.

The photochemical transformation of **2** to **1** in pressed alkali halide pellets and between CsI plates presumably occurs in a similar manner.

Finally, the quenching effect of $\mathrm{Fe(CO)}_5$ on the transformation of salted **2** into **1** ties in well with the fact that no color center formation was observed in our previous work on the CsI matrices

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of this substrate.[6] We have now searched for them again and observed only faint traces of their absorption in the visible region after the initial deposition or irradiation at 11 K. It appears very likely that Fe(CO)$_5$, and its photodecomposition products, are efficient scavengers of both H and F centers. It is then understandable that their presence will suppress the H-center-catalyzed phototransformation $\mathbf{2} \rightarrow \mathbf{1}$.

In summary, we believe that we have demonstrated the catalysis of an organic isomerization reaction by solid alkali halides, specifically, by color centers present in these solids. This has obvious implications for the use of alkali halides as "inert" matrices,[1,6] but may also be of more general interest, since catalysis by solid alkali halides is rather unusual. For instance, they were not even mentioned in a recent survey of catalysis by non-metals.[49] Some alkali halides are used as promoters in industrial heterogeneous catalysis, the mechanism of their action being quite obscure.[50] A photocatalytic effect of KBr and CsI has been reported for the photodecomposition of vinyl chloride[51] but the mechanism has not been investigated.

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Propagating Reaction Front in the Cobalt(II)-Catalyzed Autoxidation of Benzaldehyde

E. Boga, G. Peintler, and I. Nagypál*

Contribution from the Department of General and Physical Chemistry, Attila József University, H-6701 Szeged, P.O. Box 105, Hungary. Received June 19, 1989

Abstract: A propagating reaction front was found and investigated in the dissolved oxygen–Co(Ac)$_2$–benzaldehyde closed system in glacial acetic acid. The velocity of the front increases with the concentrations of benzaldehyde and dissolved oxygen and decreases with [Co(Ac)$_2$]. The experimental findings are interpreted on the basis of a simplified version of a proposed mechanism of the reaction. This is the first chemical wave reported in a nonaqueous solvent.

The liquid-phase oxidation of organic compounds by molecular oxygen catalyzed by transition metal ions has been a subject of detailed studies[1,2] for many years. Most of these reactions are autocatalytic and characterized by radical chain mechanisms. These features may result in exotic kinetic behavior, such as bistability, oscillation, and propagating reaction fronts. Oscillation has been observed and interpreted in the Co(II)-catalyzed oxidation of benzaldehyde in aqueous acetic acid in the presence of Br$^-$ ion[3,4] in an open system where the reaction mixture may take up oxygen.

The autocatalytic nature of the reaction raises the possibility of propagating reaction fronts.[5,6] Our preliminary experiments demonstrated that a propagating front could be initiated in the system by perbenzoic acid or by Co(III), which are known[7-9] intermediates of the overall reaction. The results of systematic studies of the concentration dependence of the velocity of the propagating front are reported and interpreted in the present paper.

Experimental Section

Benzaldehyde of analytical purity was distilled three times under vacuum in a nitrogen atmosphere from anhydrous K$_2$CO$_3$ and kept protected from light under nitrogen. Analytically pure, "chromic acid resistant" 99% acetic acid was freed from water with acetic anhydride. Its water content was less than 0.001%.

Co(Ac)$_2$·4H$_2$O (BDH) was purified by double recrystallization from aqueous acetic acid. It was dried to constant weight at 100 °C and 1.5 Torr, then stored over P$_2$O$_5$. Perbenzoic acid was prepared from dibenzoyl peroxide by the method of Braun.[10]

Oxygen-nitrogen mixtures (see later) were purged through an acetic acid solution of cobalt(II) acetate for 30 min through a filter containing P$_2$O$_5$ and pumice. This interval was found to be suitable for saturation of the solution. Then benzaldehyde was added, and after complete mixing the solution was pulled into a capillary tube of 1-mm internal diameter. The wave was initiated by immersing the end of the tube for a moment in a solution of 0.05 M perbenzoic acid in acetic acid. The perbenzoic acid caused the pink color of Co(II) to change to green Co(III), and this front started to travel along the tube. The propagating front was followed visually in the horizontal direction. The measurements were carried out at ambient room temperature of 22 ± 2 °C.

Results and Discussion

Figure 1 shows the distance versus time curves at four different Co(II) concentrations. The velocity of the front as a function of the concentration of the individual components is illustrated in Figures 2–4.

A quantitative characterization of the concentration dependence of the front velocity has been given only in very few cases.[5] Because of the complexity of the present system, no quantitative

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