

## Generation and Electron Spin Resonance Study of Charged Species in Rare-Gas Matrices

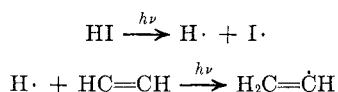
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The rare-gas matrix isolation technique is rapidly becoming a standard tool for spectroscopic characterization of reactive species. The technique consists of generating and trapping reactive species inside a frozen matrix of inert material, such as noble gases or nitrogen maintained at near liquid hydrogen or liquid helium temperature.<sup>1</sup> Reactive species generated at ambient or high temperature are mixed with a chosen inert gas and then frozen into a solid upon the surface of a cold finger.

It is also possible to generate reactive species *in situ* inside a rare-gas matrix by such a technique as photolysis, or by permitting a primary reactive species to react with a second molecule. Vinyl radicals, for example, can be produced by photolyzing HI in an argon matrix containing acetylene.<sup>2</sup>



Atoms, high-temperature molecular species, and organic free radicals have been stabilized by these methods in numerous studies and subjected to spectroscopic investigation. It has been generally assumed, however, that the rare-gas matrix isolation technique is applicable only to electrically neutral species.<sup>3</sup> Recently we have found that charged species can be generated rather readily and kept trapped within a rare-gas matrix.

(1) See, for instance, A. M. Bass and H. P. Broida, "Formation and Trapping of Free Radicals," Academic Press, New York, N. Y., 1960, or a review article by B. Mile, *Angew. Chem., Int. Ed. Engl.*, **7**, 507 (1968).

(2) E. L. Cochran, F. J. Adrian, and V. A. Bowers, *J. Chem. Phys.*, **40**, 213 (1964).

(3) There are numerous examples in which charged species are generated and trapped in amorphous organic matrices. See, for example, J. E. Willard, "Fundamental Processes in Radiation Chemistry," P. J. Ausloos, Ed., Interscience, New York, N. Y., 1969, Chapter 9. They are usually generated by energetic radiation (short uv, X- or  $\gamma$ -ray) and are stabilized by highly polar or polarized matrices. In this Account we shall be concerned only with rare-gas matrices where the matrix effects arising from dielectric constant, polarity, or polarizability are minimum.

The process developed in our laboratory consists of trapping of suitable electron-donating and electron-accepting species within the same argon matrix and then promoting an electron transfer between them by photoexcitation.<sup>4,5</sup> Let us suppose that molecules D (for donor) whose ionization potential is  $E_{IP}$  are trapped in an argon matrix at 4°K together with molecules A (for acceptor) which possess an electron affinity of  $E_{EA}$ . Let their concentrations be such that each individual molecule is isolated from the others in its ground state, but that neighboring molecules in their excited states overlap substantially (see Figure 1). In such a case it is possible to transfer an electron from molecule D to molecule A with a photoexcitation of energy  $\Delta E$  which is considerably less than the ionization potential of molecule D. It is, of course, necessary that molecule D be able to absorb the radiation corresponding to  $\Delta E$ . Once the electron is transferred, its return from the resulting anion to the cation is hampered by the local potential well imposed by the electron affinity of A, and the migration of the oppositely charged ions toward each other is prevented by the matrix lattice.

In this Account we shall review and discuss some of the results of our investigation conducted along this line. Electron spin resonance (esr) spectroscopy has been our method of detection. These experiments have enabled observation of the esr spectra of many unusual cations and anions, as well as a deeper understanding of the electron-transfer mechanism in a solid matrix.

### Experimental Methods

The details of the liquid helium Dewar and the esr spectrometer system which allows the trapping of reactive intermediates in rare-gas matrices and the measurements of their esr spectra have been reported previously.<sup>6</sup> The matrix is formed upon the surface of

(4) P. H. Kasai, *Phys. Rev. Lett.*, **21**, 67 (1968).

(5) P. H. Kasai, and D. McLeod, Jr., *J. Chem. Phys.*, **51**, 1250 (1969).

(6) P. H. Kasai, E. B. Whipple, and W. Weltner, Jr., *ibid.*, **44**, 2581 (1966).

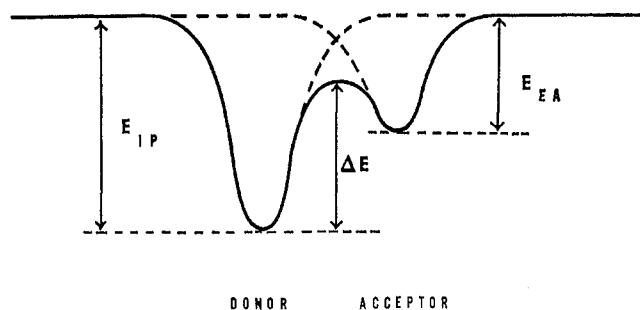


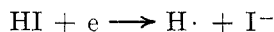
Figure 1. Overlapping of the potential curves of a donor molecule and an acceptor molecule trapped in an inert matrix.  $E_{IP}$  and  $E_{EA}$  are the ionization potential of the donor and the electron affinity of the acceptor, respectively.

a spatula-shaped sapphire rod which can be rotated about its long axis and moved vertically in and out of the esr cavity (see Figure 2). Molecules possessing a sufficiently high vapor pressure ( $>10 \mu$ ) at ambient temperature can be introduced into the matrix either by preparing a mixture with argon or through the vapor sample inlet. Solid materials with low vapor pressure are vaporized from a resistively heated stainless-steel or tantalum cell. Using a suitable combination of these appendages, argon matrices containing both the donor and acceptor species can be prepared exercising a sufficient control over their concentrations. Photoirradiation of the matrix was done through the side quartz window. A high-pressure mercury lamp (GE AH-6) equipped with an appropriate filter was the light source.

The esr spectrometer used is an extensively modified Varian Model V-4500. It incorporates a superheterodyne detection system, and the signal klystron can be locked to the sample cavity down to a power level of  $\sim 0.05 \mu\text{W}$ . This feature is particularly desirable since, at this low temperature, the signals are quite susceptible to saturation. For all the spectra reported here the frequency of the klystron locked to the loaded sample cavity was  $9432 \pm 2 \text{ MHz}$  and the optimum power level was in the range of  $5 \sim 50 \mu\text{W}$ .

### Formation of Singly Ionized Atoms

The first series of experiments was performed using certain metal atoms (Na, Cd, Cr, and Mn) as electron donors and HI as the electron acceptor.<sup>4</sup> HI has an extremely large cross section for dissociative electron capture which results in the formation of a hydrogen atom and an iodide ion.<sup>7</sup> The capture occurs with



thermal electrons and the dissociation is spontaneous. In each case metal atoms were vaporized from the resistively heated cell and trapped with argon containing 1% (by pressure) of HI. The esr of the resulting matrices were then examined before and after photoexcitation. The spectra demonstrated unequivocally

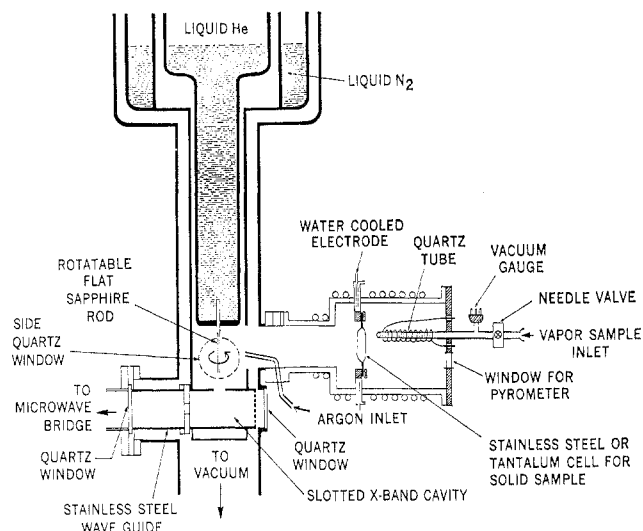


Figure 2. Cross section of the cryostat assembly consisting of a sample-rare-gas inlet section, a sapphire rod at  $4^\circ\text{K}$ , and a microwave cavity into which the sapphire rod is lowered after the formation of matrix. Photoirradiation of the matrix is done through the side quartz window.

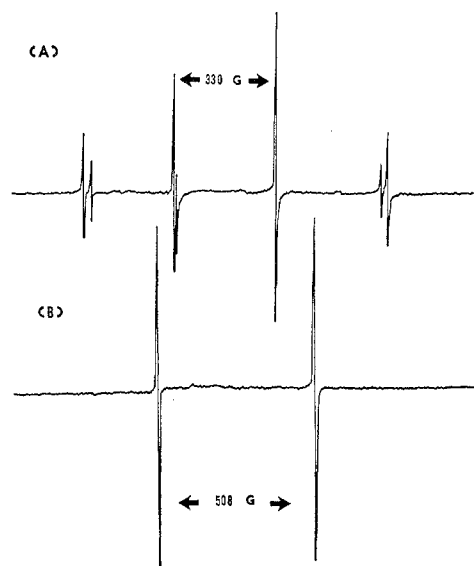


Figure 3. ESR spectra of an argon matrix containing Na atoms and HI molecules before (A) and after (B) the photoirradiation.

that the photoinduced electron transfer is possible within a solid argon matrix. The net reaction can be summarized as



The esr spectra also showed that both the starting metal atoms and the resulting singly ionized metal atoms can be considered "isolated" within the matrix.

Let us discuss briefly the highlights of the individual experiments.

**Sodium.** The esr spectra of an argon matrix containing Na and HI, obtained before and after the photoexcitation, are compared in Figure 3. The sharp quartet signal observed prior to photoexcitation with an average separation of 330 G is due to neutral Na atoms.<sup>8</sup>

(7) L. G. Christophorou, R. N. Compton, and H. W. Dickson, *J. Chem. Phys.*, **48**, 1949 (1968).

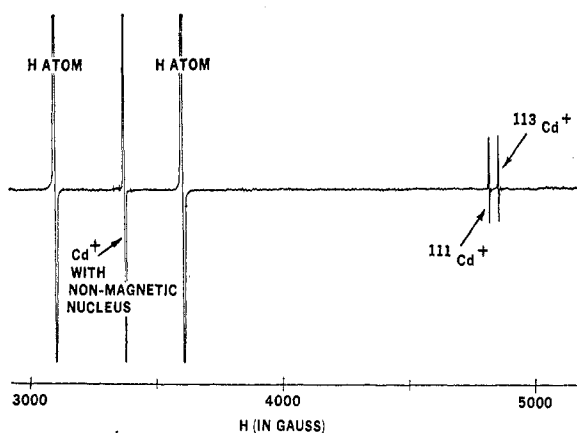


Figure 4. ESR spectrum of an argon matrix containing Cd atoms and HI molecules observed after the photoirradiation.

The ground-state electronic configuration of Na is  $3s^1$  ( $^2S_{1/2}$ ) and the quartet structure arises from a hyperfine interaction with  $^{23}\text{Na}$  nuclei (natural abundance = 100%,  $I = 3/2$ ). From the line width of the signals, the upper limit of their concentration is estimated to be about 0.1% (atom ratio). Photoirradiation of this matrix using a sharp-cutoff filter (Corning 3-70), which cuts off all the light below 5000 Å, caused a complete disappearance of the Na signals and the appearance of a strong doublet (separation 508 G) due to H atoms. No change in the esr spectrum occurred when a matrix containing Na atoms or HI molecules alone was irradiated with such light. The observed change in the spectrum, therefore, is ascribed to the photoinduced electron-transfer process



An argon matrix containing neutral Na atoms has a deep purple color owing to their d-line transitions ( $3^2S \leftrightarrow 3^2P$ , 5890 Å). For the matrix described above, an irradiation lasting for a few minutes was sufficient to bleach its color completely and to bring about a complete change in its esr spectrum. The photoirradiation, however, became totally ineffective when all the light below 6000 Å was cut off. The d-line transitions thus appear to be involved in this photoelectron-transfer process.

An interesting question is whether the resulting ions  $\text{Na}^+$  and  $\text{I}^-$  are separated from each other within the argon matrix. The answer to this question was obtained by performing the experiment using metal atoms whose singly ionized cations should be observable by esr. The atoms chosen were Cd, Cr, and Mn atoms. For these atoms, radiation of greater energy (3000 ~ 4000 Å uv light) was, however, necessary to induce the electron transfer.

**Cadmium.** No esr signal is observed from an argon matrix containing Cd and HI prior to photoexcitation. Figure 4 shows the spectrum obtained after irradiation. The strong doublet due to hydrogen atoms is easily

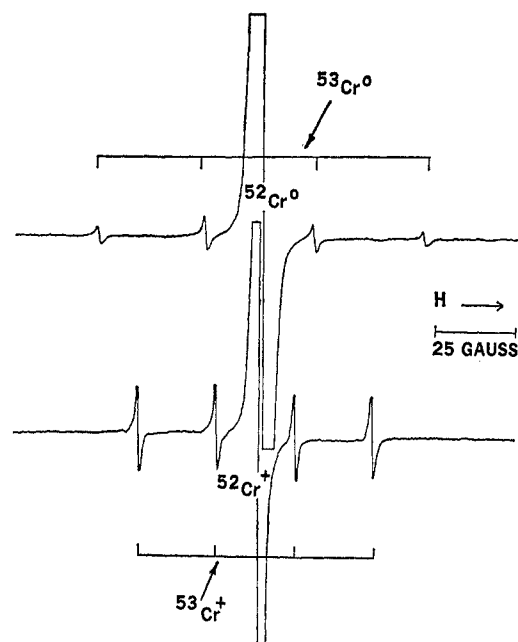


Figure 5. ESR spectra of an argon matrix containing Cr atoms and HI molecules observed before (upper trace) and after (lower trace) the photoirradiation.

recognized. The sharp signal near the center of the hydrogen doublet and the two sharp, but weaker, signals near 5000 G are assigned, respectively, to  $\text{Cd}^+$  with nonmagnetic nuclei,  $^{111}\text{Cd}^+$  (natural abundance = 12.86%,  $I = 1/2$ ), and  $^{113}\text{Cd}^+$  (natural abundance = 12.34%,  $I = 1/2$ ). The ratios of the peak-to-peak intensities of the three signals are in reasonable agreement with the ratios of the natural abundances of the isotopes involved. The  $g$  value and the hyperfine coupling constants assessed are:  $g = 2.0006 \pm 0.0002$ ;  $A(^{111}\text{Cd}^+) = 5137 \pm 1$  G or 14.385 GHz;  $A(^{113}\text{Cd}^+) = 5374 \pm 1$  G or 15.048 GHz. The hfs constants obtained here give 1.0461 as the ratio of the magnetic moments of the two nuclei,  $^{113}\text{Cd}$  and  $^{111}\text{Cd}$ , in exact agreement with the known value. The lower field components of the doublets normally expected from the hyperfine interaction with a nucleus of spin  $1/2$  are not observed here because these coupling constants are larger than the microwave frequency of the spectrometer. The closeness of the  $g$  value to the free spin value (2.0023) and the extremely large, isotropic hfs constants are consistent with the electronic configuration  $4d^{10}s^1$  ( $^2S_{1/2}$ ) expected of a singly ionized Cd atom. Another important fact is that there is no evidence in the observed spectrum of any significant interaction with another magnetic nucleus such as  $^1\text{H}$  (natural abundance  $\cong 100\%$ ,  $I = 1/2$ , magnetic moment = 2.793 nuclear magneton) or  $^{127}\text{I}$  (natural abundance = 100%,  $I = 5/2$ , magnetic moment = 2.794). The sharpness of the observed signal ( $\Delta H$  peak-to-peak  $\cong 0.3$  G) indicates that there is no such magnetic nucleus within  $\sim 5$  Å of the singly ionized metal atoms.

**Chromium.** The spectra observed before and after the photoexcitation are compared in Figure 5. In each trace, the strong central signal is accompanied by a

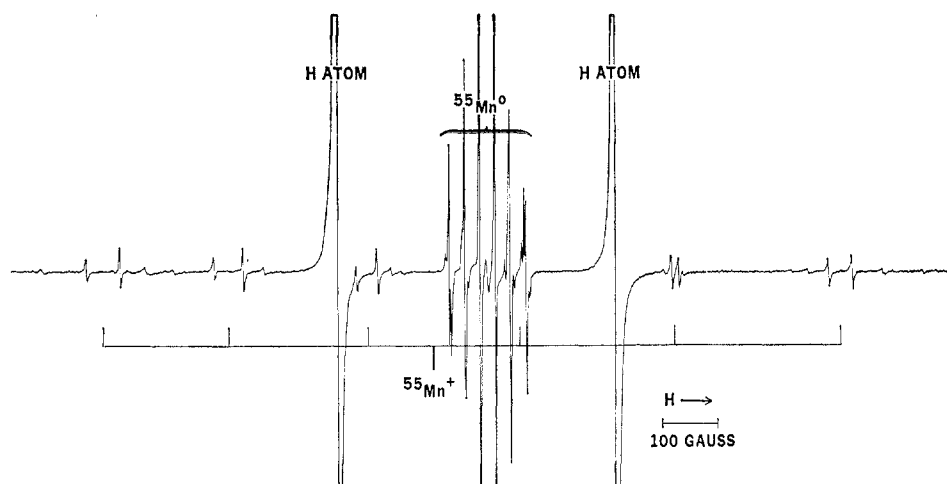


Figure 6. Esr spectrum of  $\text{Mn}^0$  and  $\text{Mn}^+$  in an argon matrix at  $-4^\circ\text{K}$ .

Table I

Atoms	IP, eV	Atoms	IP, eV
Na	5.14	Mg	7.65
Eu	5.67	Cd	8.99
Cr	6.76	Zn	9.39
Mn	7.43	Hg	10.43

weak equally spaced quartet, hyperfine structure due to  $^{53}\text{Cr}$  (natural abundance = 9.55%,  $I = 3/2$ ). The ground-state electronic configurations of  $\text{Cr}^0$  and  $\text{Cr}^+$  are  $3d^5 4s^1$  ( ${}^7\text{S}_3$ ) and  $3d^5$  ( ${}^6\text{S}_{5/2}$ ), respectively. The  $g$  values of both  $\text{Cr}^0$  and  $\text{Cr}^+$  are, therefore, expected to be very close to that of a free electron, and the spectra should be free of "fine structure" provided they are not subjected to a crystal field with a symmetry less than that of a cubic field. The fine-structure interactions are anisotropic (orientation dependent), and the sharpness of the observed spectra clearly defies the possibility that diatomic molecular species such as  $\text{CdH}$  or  $\text{CdI}$  are responsible for the observed signals. The difference in the hfs spacing of the  $^{53}\text{Cr}$  satellites before and after the photoexcitation is quite conspicuous. Accordingly, the spectra are assigned to isolated  $\text{Cr}^0$  atoms and  $\text{Cr}^+$  ions, respectively. The most remarkable aspect of this experiment is that it is setting forth a direct evidence for a total conversion of neutral atoms into singly ionized form.

**Manganese.** Figure 6 shows the spectrum observed with Mn after the photoexcitation. It shows both the spectrum due to  $\text{Mn}^0$  which, of course, was observed before the irradiation and the spectrum attributed to  $\text{Mn}^+$  which appeared only after the irradiation. The small hfs constant (27.9 G) of  $\text{Mn}^0$  and the large hfs constant (270.4 G) of  $\text{Mn}^+$  are consistent with the ground-state electronic configurations of  $\text{Mn}^0$  and  $\text{Mn}^+$ ,  $3d^5 4s^2$  ( ${}^6\text{S}_{5/2}$ ) and  $3d^5 4s^1$  ( ${}^7\text{S}_3$ ), respectively. A multiple structure within each hyperfine group of  $\text{Mn}^+$  is due to an "incomplete" Paschen-Back effect and is not due to a crystal field effect. A doublet-like appearance prominent in each group is due to the transitions  $M_s = 1 \leftrightarrow 0$  and  $M_s = 0 \leftrightarrow -1$ .

Because of the nature of the experiment, it is difficult

to make a quantitative comparison of the results obtained here among different atoms. However, a comparison of the manners and the extents to which these atoms have been ionized reveals immediately an expected trend relating to their ionization potentials. Listed in Table I are the ionization potentials of the atoms<sup>9</sup> discussed above and some of others which we have also investigated. Thus, when the concentration of HI in argon was maintained at 1%, atoms such as Na or Eu were converted completely to singly ionized form with mere "visible" light. For atoms Cr through Zn in Table I irradiation with uv light was necessary for the ionization. In the case of Cr, a complete conversion was achieved with 10 min of irradiation in contrast to the case of Mn (and probably of others) for which a complete conversion was never achieved. In the case of Hg, we failed to see any signal attributable to singly ionized species.

### Formation of Molecular Anions

The facility with which we have succeeded in promoting an electron transfer between metal atoms and HI molecules immediately prompts a chemist to speculate on the possibility of generating molecular anions. One particular point of concern, however, was that species as small as metal atoms or HI molecules could well be incorporated within the argon lattice substitutionally and the periodic potential provided by the lattice might somehow be facilitating the observed electron-transfer process. Given below are brief accounts of the experiments conducted using Na atoms as electron donors and tetracyanoethylene (TCNE),  $\text{B}_2\text{H}_6$ , and furan molecules, respectively, as the acceptors. In this particular series of experiments, a sharp cutoff filter, Corning 3-70, was used, and hence the matrix was irradiated only with "yellow" light ( $\lambda > 5000 \text{ \AA}$ ). That we have observed the electron-transfer process involving molecules as large as TCNE or furan clearly indicates that the process does not require a continuity in the periodic potential of the surrounding matrix.

(9) R. C. Weast, "Handbook of Chemistry and Physics," 50th ed, The Chemical Rubber Co., Cleveland, Ohio, 1969.

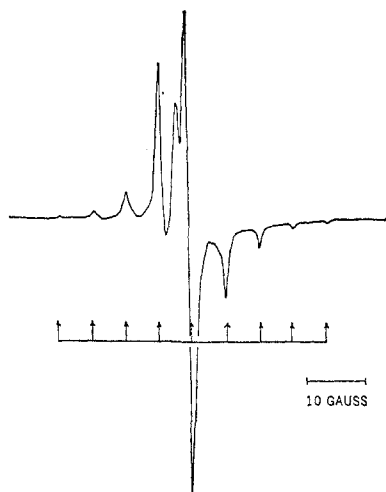
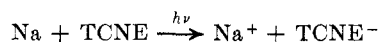


Figure 7. ESR spectrum of tetracyanoethylene anion (TCNE) generated in an argon matrix. The arrows indicate the nine "parallel" components caused by the couplings to the four equivalent  $^{14}\text{N}$  nuclei.

**Tetracyanoethylene.** TCNE is well known for its large electron affinity (3.25 eV), and the corresponding anion radicals can be readily prepared in solution at ambient temperature. The esr spectrum of the radicals in solution consists of nine equally spaced lines with the characteristic intensity pattern consistent with a hyperfine interaction with four equivalent  $^{14}\text{N}$  nuclei ( $I = 1$ ).<sup>10</sup> Prior to the photoirradiation, the esr spectrum of an argon matrix containing both Na and TCNE consisted of the Na quartet and a weak broad signal centered about the position corresponding to  $g = 2.0$ . Irradiation of this matrix resulted in a complete disappearance of the Na signals and a severalfold increase of the signals at  $g = 2.0$  (see Figure 7). The photoinduced signal is attributed to TCNE anion radicals resulting from the electron-transfer reaction



The overall pattern of this spectrum has the characteristics expected from randomly oriented radicals possessing an axially symmetric, but extremely anisotropic, hyperfine coupling tensor,  $A_{\parallel} \gg A_{\perp} \cong 0$ . The following values were assessed from the spectrum:  $g_{\parallel} = 2.0023 \pm 0.0001$ ,  $g_{\perp} = 2.0030 \pm 0.0005$ ,  $A_{\parallel}(^{14}\text{N}) = 5.7 \pm 0.1$  G, and  $A_{\perp}(^{14}\text{N}) = 0 \pm 0.2$  G. The nine signals assigned to the "parallel" components are quite discernible as indicated in the figure.<sup>11</sup> The analysis of the anisotropy of the  $A$  tensor gives a spin density of 0.11 at the  $2p_{\pi}$  orbital of each nitrogen.

**Diborane.**<sup>5</sup> Although the boron hydrides are known as "electron-deficient" molecules, because of their extreme reactivity, no esr study of their anions had been reported previously. The esr spectrum of diborane

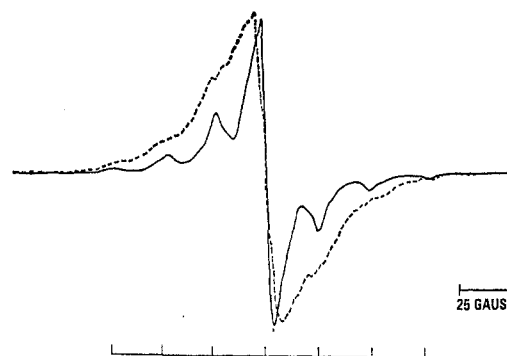


Figure 8. ESR spectra photoinduced from the matrix containing  $\text{B}_2\text{H}_6$  (dotted line) and  $^{11}\text{B}_2\text{D}_6$  (solid line).

anion, for example, should be very elucidative since a large number of theoretical treatments have been performed concerning the nature of the bondings involved in this molecule. We therefore prepared an argon matrix containing Na atoms and  $\text{B}_2\text{H}_6$ . Prior to the photoirradiation, the esr spectrum of this matrix consisted of the Na quartet only. The photoexcitation caused a complete disappearance of the quartet and an appearance of a broad signal ( $\Delta H_{1/2} \cong 70$  G) at the position corresponding to  $g = 2.0$ . A careful examination of this photoinduced signal indicated the existence of several shoulders arranged symmetrically about the center of the signal, suggesting a hyperfine interaction due to two equivalent  $^{11}\text{B}$  nuclei (natural abundance = 81%,  $I = 3/2$ ). The experiment was repeated, therefore, using  $^{11}\text{B}_2\text{D}_6$ , enriched in both  $^{11}\text{B}$  ( $\sim 100\%$ ) and D ( $\sim 100\%$ ) isotopes.<sup>12</sup> The photoinduced signal obtained from  $^{11}\text{B}_2\text{D}_6$  is compared with that obtained from normal  $\text{B}_2\text{H}_6$  in Figure 8. A septet pattern expected from the hyperfine interaction with the two equivalent  $^{11}\text{B}$  nuclei is clearly resolved in the spectrum obtained from  $^{11}\text{B}_2\text{D}_6$ . In a manner similar to the case of TCNE anions, the overall pattern of this spectrum has the characteristics expected from randomly oriented radicals possessing an axially symmetric but highly anisotropic hyperfine coupling tensor ( $A_{\parallel} \gg A_{\perp} \cong 0$ ). The analysis of the spectrum yielded the following parameters:  $g_{\parallel} = g_{\perp} = 2.0020 \pm 0.0005$ ,  $A_{\parallel}(^{11}\text{B}) = 24.5 \pm 0.5$  G,  $A_{\perp}(^{11}\text{B}) \leq 3.0$  G, and  $A(\text{H}) \leq 15$  G. According to a recent SCF-LCAO calculation of  $\text{B}_2\text{H}_6$  by Palke and Lipscomb,<sup>13</sup> the unpaired electron in  $\text{B}_2\text{H}_6^-$  should occupy a  $b_{2g}$  orbital given by an antibonding combination of the boron 2p orbitals perpendicular to the plane defined by the four terminal hydrogen atoms (note that all six protons are at the nodal planes of this orbital). The observed results, a highly anisotropic coupling to the boron nuclei and a small coupling to any particular proton, are consistent with this model. They are not compatible with the lowest unoccupied orbitals predicted by the

(10) W. D. Phillips, J. C. Rowell, and S. I. Weissman, *J. Chem. Phys.*, **33**, 626 (1960).

(11) For methods of analysis of an esr pattern arising from randomly oriented paramagnetic species, see, for example, P. W. Atkins and M. C. R. Symons, "The Structure of Inorganic Radicals," Elsevier Publishing Co., Amsterdam, 1967, Appendix 5.

(12) We are indebted to Dr. T. Coyle (National Bureau of Standards) for this material.

(13) W. E. Palke and W. N. Lipscomb, *J. Chem. Phys.*, **45**, 3948 (1966).

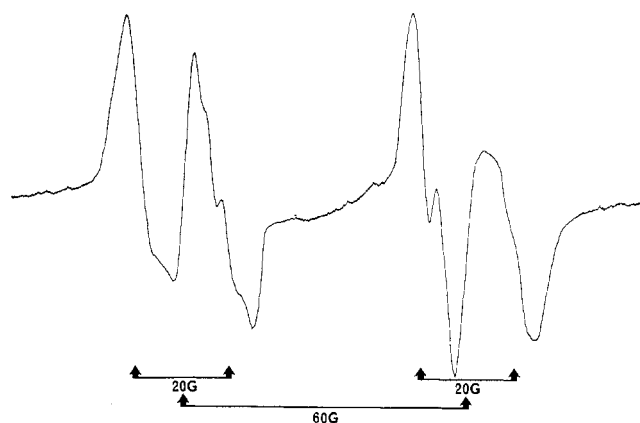
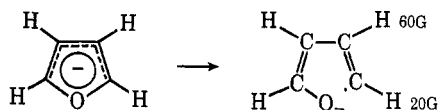


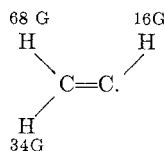
Figure 9. ESR spectrum of furan "anion" generated in an argon matrix. See text for the structure of the anion.

earlier SCF calculation of Hamilton<sup>14</sup> or Yamazaki.<sup>15</sup>

**Furan.** Shown in Figure 9 is the esr spectrum obtained after photoirradiation of an argon matrix containing Na and furan. The spectrum is essentially a doublet of doublets. The most extraordinary feature of this spectrum is the magnitude of the larger doublet spacing. A coupling constant of 60 G is much too large for any interaction expected for a  $\pi$  anion radical. We propose, therefore, that the spectrum is due to  $\sigma$  anion radical resulting from spontaneous ring opening of furan anions.



The observed splittings of 20 and 60 G are assigned, respectively, to  $\alpha$  and  $\beta$  protons in the open structure as indicated. The anion radical with the open structure may be considered as a substituted vinyl radical. The isotropic coupling constants reported for various protons in vinyl radicals are<sup>2</sup>



The proximity of the coupling constants observed in "furan anion" to those of  $\alpha$  and trans- $\beta$  protons in vinyl radicals is a strong support for the proposed structure.

We have thus shown that photoelectron transfer in an argon matrix involving molecular species can also be realized. As demonstrated by the examples described above, the technique may be utilized (1) to assess the anisotropy of the hyperfine and/or the  $g$  tensors of an anion radical to supplement the result of a solution study, or (2) to generate a new anion radical of a species which is too reactive to handle under ordinary condi-

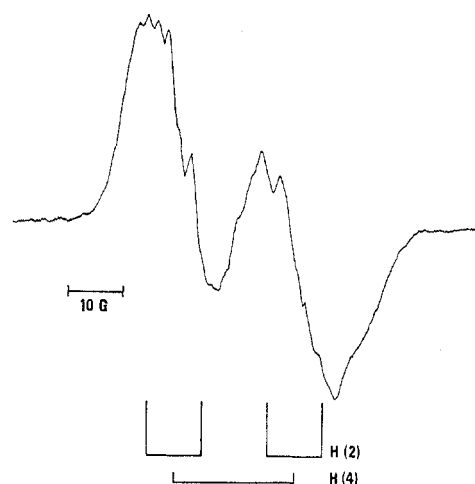
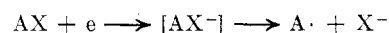


Figure 10. ESR spectrum of an argon matrix containing Na atoms and 3-chloropyridine observed after the photoirradiation. Shown below is the spectrum pattern of 3-pyridyl radical predicted by INDO.

tions, and finally (3) to elucidate the structure of anion radicals which no longer possess the integrity of the neutral state and would be too reactive to be detected in a fluid system.

#### Formation of Neutral Radicals by Dissociative Electron Capture

A dissociative electron capture is a well-known process when a molecular beam encounters an electron beam. For halogenated molecules passing through a swarm of electrons it is often the dominant process and leads to the formation of a neutral radical and a halide ion.<sup>16,17</sup> Could this process also occur in an inert ma-



trix at near liquid helium temperature when electrons are transferred to these molecules by our technique, and be utilized for generation of neutral radicals? Dissociation of  $HI^-$  into a hydrogen atom and  $I^-$  ion described in the earlier section is clearly a successful example. The cross section for dissociative electron capture by  $HI$  molecules, however, is at least two orders of magnitude larger than those of other halogenated molecules.<sup>17</sup> We will therefore discuss the results obtained when electrons are transferred from Na atoms to fluorobenzene and 3-chloropyridine, respectively, in an argon matrix. Again, in this series of experiments, only the "yellow light" ( $\lambda > 5000 \text{ \AA}$ ) was used for the irradiation.

**Fluorobenzene.** The photoirradiation of an argon matrix containing Na and fluorobenzene results in a disappearance of the Na quartet and an appearance of the signals due to phenyl radicals.<sup>18</sup> Clearly what has occurred in the photoelectron-transfer process is a dissociative electron capture of the type anticipated above.

(16) L. G. Christophorou and R. N. Compton, *Health Phys.*, **13**, 1277 (1967).

(17) L. G. Christophorou and J. A. D. Stockdale, *J. Chem. Phys.*, **48**, 1956 (1968).

(18) P. H. Kasai, E. Hedaya, and E. B. Whipple, *J. Amer. Chem. Soc.*, **91**, 4364 (1969).

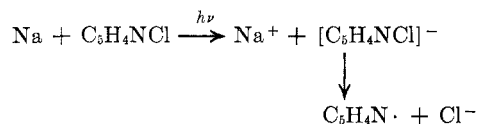
(14) W. C. Hamilton, *Proc. Roy. Soc., Ser. A*, **235**, 395 (1956).

(15) M. Yamazaki, *J. Chem. Phys.*, **27**, 1041 (1957).



One should note that here the phenyl radicals are generated under the influence of mere "yellow light," while  $\text{C}_6\text{H}_5\text{F}$  itself is stable even against uv irradiation.

**3-Chloropyridine.**<sup>19</sup> Figure 10 shows the spectrum obtained after the photoirradiation of an argon matrix containing Na and 3-chloropyridine. The spectrum is attributed to 3-pyridyl radicals resulting from the reaction



The plausibility of the anion formation has already been established. The structure resolved, however, indicates a hyperfine interaction which is much too large for a  $\pi$  radical anion. It can be easily understood if the spectrum is assigned to a  $\sigma$  radical resulting from a spontaneous dissociation of the anion as proposed above. Depicted below the observed spectrum is the spectral pattern of the 3-pyridyl radical calculated by the INDO molecular orbital theory.<sup>20</sup> The general agreement between the calculated pattern and the observed spectrum strongly substantiates the assignment. The observed doublet pattern of 22 G is thus assigned to the hfs due to proton 4. Prior to these experiments we had attempted to generate the same radicals by direct uv photolysis ( $\lambda < 4000 \text{ \AA}$ ) of 3-pyridyl iodide. In this case we observed mainly the radicals resulting from a process involving a rupture of the aromatic ring. Irradiation with uv of a matrix containing pyridyl radicals generated by the photoelectron-transfer process resulted in a disappearance of the spectrum shown above and an appearance of the spectrum identical with that obtained by direct photolysis of the iodide. Thus the rupturing of the ring appears to be a result of a photolytic process imposed on pyridyl radicals.

The results described above clearly demonstrate that, at least for halogenated molecules, the process of dissociative electron capture occurs quite easily even in a rigid rare-gas matrix at liquid helium temperature and can be readily utilized for the purpose of generating neutral radicals. The most exciting aspect of this approach is that it appears to be a much more gentle way of cleaving a carbon-halogen bond than a direct photolysis. Thus, radicals which would not be stable against uv irradiation can be generated and trapped by this technique, providing opportunities not only to conduct spectroscopic characterization of the radicals but also to examine their photolytic sequences.

### Concluding Remarks

The various examples presented in the foregoing sections convincingly demonstrate that, by means of a photoexcitation, an electron can be transferred from an electron-donating species to an acceptor within a rare

(19) P. H. Kasai and D. McLeod, *J. Amer. Chem. Soc.*, **92**, 6085 (1970).

(20) J. A. Pople, D. L. Beveridge, and P. A. Dobosh, *J. Chem. Phys.*, **47**, 2026 (1967); *J. Amer. Chem. Soc.*, **90**, 4201 (1968).

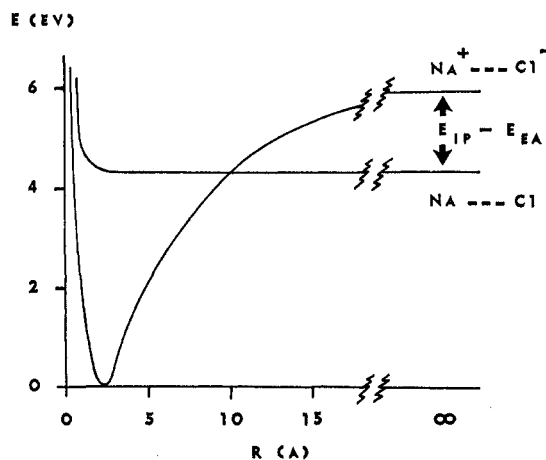


Figure 11. The potential curve of the states resulting from an approaching neutral Na atom-Cl atom pair and that resulting from the corresponding ions,  $\text{Na}^+$  and  $\text{Cl}^-$ .

gas matrix at 4°K, resulting in a formation of charged species "effectively isolated" within the matrix. One feature which has consistently amazed us throughout these experiments is the facility with which such an electron transfer can be accomplished. In this final section we shall make an attempt to shed some light on this aspect. Let us consider an electron-donating species D and an accepting species A separated by a distance  $R$  within a rigid argon matrix. For the sake of simplicity we shall assume that the sole function of the host matrix is to keep the species rigidly fixed at their respective positions, neglecting all other influences it may have upon the transfer process. The energy required to transfer an electron from D to A is then given by

$$\Delta E = E_{\text{IP}}(\text{D}) - E_{\text{EA}}(\text{A}) - \frac{e^2}{\epsilon R}$$

where  $E_{\text{IP}}(\text{D})$  and  $E_{\text{EA}}(\text{A})$  are the ionization potential of the donor and the electron affinity of the acceptor, respectively, and  $\epsilon$  is the dielectric constant of Ar. The last term in this expression represents a Coulombic potential energy between the resulting anion-cation pair. A typical condition in our experiments was that the argon matrix contained approximately 0.1% (atomic ratio) of the donors, say Na atoms, and 1% of the acceptors, say  $\text{B}_2\text{H}_6$ . Argon is known to crystallize in a face-centered-cubic form with a unit cell dimension of 5.308 Å. A simple calculation then shows that an acceptor concentration of 1% amounts to placing one acceptor molecule within each spherical volume of 10-Å radius. The "average" separation between a donor and its nearest acceptor in our typical matrix is therefore estimated to be 7 ~ 8 Å. At this separation the Coulombic term given above becomes as large as 2 eV. Hence if the chosen acceptor possesses an electron affinity of ~1 eV or larger, it should be entirely possible to "ionize" Na atoms ( $E_{\text{IP}} = 5.18 \text{ eV}$ ) only with "yellow" light corresponding to a  $\Delta E$  of ~2.5 eV.

The same explanation can be put forward in a some-

what more dramatic fashion by comparing a well-known potential curve of the states resulting from a neutral sodium atom and chlorine atom approaching from an infinite separation with the curve resulting from the corresponding cation-anion pair<sup>21</sup> (see Figure 11). The drop in the potential curve for the approaching  $\text{Na}^+ \cdots \text{Cl}^-$  pair is due to none other than the Coulombic term,  $-e^2/R$ . According to this figure, if a neutral sodium atom and a chlorine atom are somehow brought together and held at a separation of  $10 \text{ \AA}$  or less, an electron should spontaneously transfer from the Na to Cl atom! Furthermore a recent computer calculation shows that, after such an electron transfer, the electron distributions about each of the resulting ions are very close to those of the free ions,<sup>22</sup> in a complete agreement with our experimental finding.

(21) G. Herzberg, "Spectra of Diatomic Molecules," Van Nostrand, Princeton, N. J., 1950.

(22) See, for example, A. C. Wahl, *Sci. Amer.*, **222** (4), 54 (1970).

Argon atoms between the donor and the acceptor pair may impose a barrier against a spontaneous electron transfer, thus creating a need for photoexcitation. For most of the experiments described in this article, the ionization potential of the donor and the electron affinity of the acceptor are such that, at the separation of  $7 \sim 8 \text{ \AA}$ , the electron-transfer process as envisaged above is still endothermic. In these cases, an important role of argon atoms must be the formation, through polarization, of a potential barrier and a trap about the resulting cation and anion, respectively, thus preventing a spontaneous return of the electron. The situation is then very similar to that depicted in Figure 1.

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