Studies of Isotopic Exchange in Solid State: Healing of Damaged Molecules

Amar Nath

Department of Chemistry, Drexel University, Philadelphia, Pennsylvania 19104

When solid K_2CrO_4 is irradiated with thermal neutrons in a reactor, the chromium atom absorbs a neutron and energetic γ photons are emitted, $^{50}Cr(n,\gamma)^{51}Cr$. Conservation of momentum requires that the radioactive atom ^{51}Cr undergo violent recoil (involving almost 100 eV) tearing away from the parent molecule. Chemical analysis of the irradiated material shows that the ^{51}Cr activity is found primarily in two fractions, namely, $^{51}Cr^{3+}$ and $^{51}CrO_4^{2-}$. The percent activity in the form of the parent species, namely, $^{51}CrO_4^{2-}$ is termed retention. Green and Maddock[1] observed that if the irradiated K_2CrO_4 is heated prior to dissolution in water for chemical analysis, then the retention increases, i.e., the neutron-irradiated material undergoes thermal annealing. This thermal annealing was also observed for irradiated permanganates, iodates, bromates, and later for metal complexes. Typical isothermal annealing plots are shown in Figure 1.

The thermal annealing was widely interpreted on the basis of recombination of fragments formed by the recoil atom,[2] not only for oxyanion systems but also for compounds like $K_3[Co(CN)_6]$[3] and hexachloro and hexabromo complexes of iridium and osmium.[4] For instance, the thermal annealing in cobalticyanide was attributed to the following reactions involving fragments:

$$^{60}Co(CN)_4^- + CN^- \rightarrow {}^{60}Co(CN)_5^{2-}$$

$$^{60}Co(CN)_5^{2-} + CN^- \rightarrow {}^{60}Co(CN)_6^{3-}$$

$^{60}Co(CN)_4^-$ degrades during the analytical separation and manifests itself as $^{60}Co^{2+}$, while after thermal treatment, according to the proposed scheme, the $^{60}Co(CN)_4^-$ is converted into $^{60}Co(CN)_6^{3-}$ and constitutes part of retention. However, our thinking was conditioned by thermal annealing studies on cobalt chelates possessing multidentate ligands, including hexadentate ligands like EDTA.[5-7] In these chelates, it is difficult to visualize such neat reconstitution of the parent complex and with such high efficiency, from fragments, by thermal treatment.

The first important lead toward understanding of the mechanism of thermal annealing of recoil damage came about with the observation of the "oxygen effect". We found that when irradiated cobalt chelates are heated in vacuum or in an inert atmosphere, the annealing progresses much faster than in air.[8-10] We proposed that the oxygen molecules adsorbed on the surface of the microcrystallites act as electron traps and suppress

annealing. We heated aliquots of irradiated tris(acetylacetonato)cobalt(III) in air at a specified temperature, say 110 °C, until the retention acquired a maximum value, R_∞. If we then pumped on the samples at room temperature and then heated them again at 110 °C, further annealing took place as shown in Figure 2. Later, we found that electron-donating ambients like gaseous acetone and alcohol enhance the rate of annealing in neutron-irradiated bis(salicylaldehydato)-(triethylenetetramine)cobalt(III) chloride, while electron-accepting ambients like O_2 and NO retard it.[11] We proposed that electrons participate in the process of annealing and that electrons are captured or injected at the particle interface by adsorbed molecules of the ambient.

Where do the electrons, which trigger thermal annealing of recoil damage in substances, come from? We proposed that the cobalt chelates and other systems discussed above are wide-band semiconductors and the defects and impurities present in the crystallites can serve as electron donors having differing depths, i.e., traps binding electrons with differing energies. Electrons can be detrapped (released) on thermal activation.[9] These ideas were supported by observations made by Andersen and Olesen[12] on neutron-irradiated K_2CrO_4. They observed a correlation between thermal annealing vs. thermally stimulated luminescence and conductivity "glow curves", showing that thermal annealing is associated with the release of trapped electrons (or holes).

The main question, however, concerns the nature of the process that, with the help of free electrons, transforms degraded radioactive recoil species into the parent compound, i.e., recoil species + electron(s) → parent compound. Several early researchers[2,13,14] had considered isotopic exchange as a likely process in thermal annealing, although the first experimental observation was reported by Kaucic and Vlatkovic.[15]

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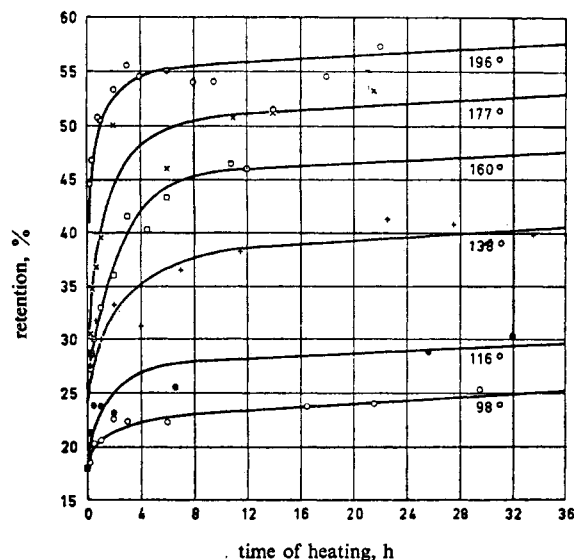
Figure 1. Isothermal annealing curves for anhydrous calcium bromate (reproduced with permission from *Trans. Faraday Soc.* 1960, *56*, 511. Copyright Faraday Society, 1960).
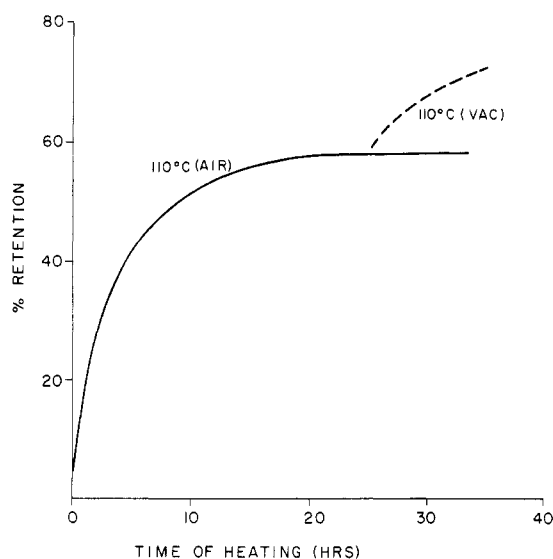

Figure 2. Isothermal annealing for neutron-irradiated tris(acetylacetonato)cobalt(III) in air at 110 °C and followed by annealing at the same temperature but in vacuum.

They doped crystals of calcium iodate with a trace of radioactive $^{131}I^-$ and heated the material at relatively high temperatures (200–400 °C). They found that a fraction of the radioiodide activity becomes incorporated into the iodate form. They suggested that the thermal annealing in neutron-irradiated iodate could be explained to a certain extent by exchange reactions. Similar experimental observations were made by Apers et al.[16] for K_2CrO_4 doped with $^{51}Cr^{3+}$. They termed the incorporation of activity in the chromate form due to heating as "transfer annealing"—a process, according to them, that may involve an oxidation of the tracer species and is not necessarily an isotopic exchange. In a subsequent publication,[17] the same group of researchers considered several possible mechanisms for oxidation of the dopant, $^{51}Cr^{3+}$, resulting in the for-

mation of intermediate species that on dissolution in water could form the parent chromate. Incorporation of activity into the chromate by isotopic exchange was disregarded.

Two possible mechanisms were considered by Collins et al.[17] for the oxidation of Cr^{3+}. First, mobile exciton produced in the bulk crystal could deposit energy at the site of the dopant $^{51}Cr^{3+}$ and trigger a donation of an oxygen atom to the chromium-51 from an adjacent chromate ion. Alternatively, CrO_4^- might be formed

$$^{51}Cr^{3+} + CrO_4^{2-} \rightarrow {}^{51}CrO^{3+} + CrO_3^{2-}$$
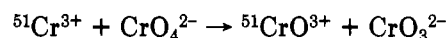
as a result of thermal ionization of CrO_4^{2-}, and some of the free electrons are trapped. The CrO_4^- could diffuse in the lattice by a hole conduction mechanism. The diffusing CrO_4^- (hole) may then encounter a dopant ion $^{51}Cr^{3+}$ and oxidize it to $^{51}Cr^{4+}$. Several such sequential

$$CrO_4^- + CrO_4^{2-} \rightarrow CrO_4^{2-} + CrO_4^-$$

$$^{51}Cr^{3+} + CrO_4^- \rightarrow {}^{51}Cr^{4+} + CrO_4^{2-}$$
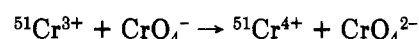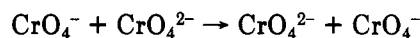
steps, according to their mechanism, are necessary before the chromium-51 species would manifest as radiochromate during dissolution for analysis. Similar scepticism regarding isotopic exchange being responsible for "transfer annealing" and its possible role in thermal annealing of recoil effects was expressed by Harbottle[2] and Maddock and Andersen.[18]

Scepticism among hot atom chemists persisted for several reasons. First, experimental evidence for thermal exchange in systems other than simple oxyanions like iodate and chromate was lacking. As discussed above, one did not have to invoke isotopic exchange to understand the transformation of $^{51}Cr^{3+}$ to $^{51}CrO_4^{2-}$. Secondly, isotopic exchange in solids involves breaking of strong coordination bonds and is expected to be associated with large activation energies, while thermal annealing of recoil effects can take place at low temperatures. Thirdly, several reaction components were observed in thermal annealing, while for thermal exchange between radioactive recoil species and an inactive parent molecule, one expects a single first-order component.[19] Fourthly, the relation between defects in solids, known to play an important role in thermal annealing,[20-25] and isotopic exchange was not apparent.

Electronically Excited Isotopic Exchange

Sometime ago we[26] showed that isotopic exchange can occur even in cobalt chelates doped with radiocobalt-(2+). It is not possible to interpret the incorporation of cobalt activity in the chelate form by oxidative

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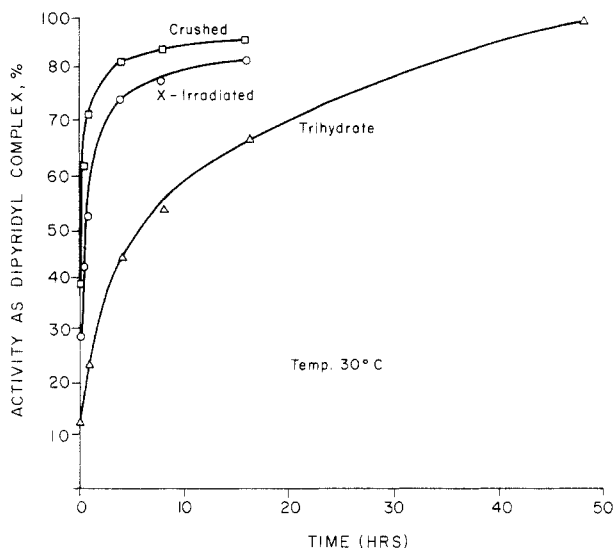(26) Nath, A.; Khorana, S.; Mathur, P. K.; Sarup, S. *Indian J. Chem.* 1966, *4*, 51.

Figure 3. Isotopic exchange in tris(dipyridyl)cobalt(III) perchlorate doped with $^{57}Co^{2+}$ without any prior treatment and after X-irradiation and mechanical crushing of the material.

mechanism involving holes suggested for the K_2CrO_4–$^{51}Cr^{3+}$ system,[16,17] so we came to regard the incorporation of activity in the chelate form as arising through genuine isotopic exchange. Our model for this takes into consideration the following features.

(a) Exchange in the solid state can occur even at relatively low temperature. For instance, exchange occurs in $^{57}Co^{2+}$-doped tris(dipyridyl)cobalt(III) perchlorate[26] and tris(phenanthroline)cobalt(III) perchlorate[27] at an appreciable rate at room temperature. Occurrence of exchange at low temperatures is amazing in view of the fact that exchange involves transfer of the ligands from the inactive central atom to the radiodopant, which entails breaking of strong coordination bonds. One would expect that the exchange be governed by large activation energies.[2] The proposed model should adequately account for the source of energy.

(b) Electron-accepting ambients of oxygen and nitric oxide were also found to affect the rate of exchange in several $^{57}Co^{2+}$-doped cobalt chelates,[26,28,29] in a fashion similar to that of thermal annealing.

Mechanical crushing and X-irradiation induces exchange[26] (Figure 3) and also annealing of recoil damage.[20–26,30] Several substances are known to emit exo electrons during crushing (plastic deformation).[31,32] X- or γ-irradiation also excite electrons in the conduction band. One can infer from these observations that free electrons (or holes) participate not only in thermal annealing of recoil damage but also in isotopic exchange.

(c) For strong field ligand chelates, e.g., dipyridyl and o-phenanthroline complexes, exchange between radiocobalt(2+) and the cobalt chelate has not been detected in aqueous solutions. This shows that the observed exchange in solid metal chelates is specifically a solid-state phenomenon.

On the basis of the afore-discussed observations, we[26,33] have proposed the "electronically excited isotopic exchange" model. An important feature of the model is that the excitation energy required to induce isotopic exchange or thermal annealing in the solid state is derived from the interaction of a free electron (or hole) with the radiodopant or recoil species. To exemplify, let us consider the isotopic exchange between the dopant $^{57}Co^{2+}$ and $[Co(III)(dipy)_3(ClO_4)_3]\cdot 3H_2O$, where dipy = α,α'-dipyridyl. The crystal defects in the chelate loosely bind electrons and constitute multidepth electron donors. A thermally detrapped electron interacts with $^{57}Co^{2+}$ to form electronically excited $*^{57}Co^+$. The dopant ion interacts weakly with neighboring molecules(s) to form a loosely bound structure and enables the electronic excitation energy to be partly converted into vibratioinal energy through radiationless transition.[34] An electron is probably transferred from $*^{57}Co^+$ to the Co(III) complex molecule. The partial conversion of electronic excitation into vibrational energy and the fact that the Co(III) chelate molecule is reduced to Co(II) considerably enhances the mobility of the ligands, facilitating their transfer onto the vibronically excited $*^{57}Co^{2+}$. The electron residing in $^{57}Co(II)$ chelate molecule is delocalized among neighboring Co(III) chelate molecules as they constitute a mixed-valence environment.

$$e^-(\text{trap}) + \text{phonons} \rightarrow e^-(\text{free})$$

$$^{57}Co^{2+} + e^- \rightarrow *^{57}Co^+$$

$$*^{57}Co^+ + [Co(III)(dipy)_3]^{3+} \rightarrow$$
$$*^{57}Co^{2+}[Co(II)(dipy)_3]^{2+}$$

$$*^{57}Co^{2+}[Co(II)(dipy)_3]^{2+} \rightarrow$$
$$[*^{57}Co(II)(dipy)_3]^{2+} + Co^{2+}$$

$$[*^{57}Co(II)(dipy)_3]^{2+} + [Co(III)(dipy)_3]^{3+} \rightarrow$$
$$[^{57}Co(III)(dipy)_3]^{3+} + [Co(II)(dipy)_3]^{2+}$$

The probability of the electronically excited dopant undergoing exchange with the complex molecule is presumably determined by the nature and stereochemistry of the complex moiety and the site of the dopant vis-a-vis the complex. The dopant may or may not be mobile.[35] If the dopant is immobile, one cannot attain isotopic exchange beyond 50%. Since the large activation energy required for the exchange is derived from the interaction energy of the dopant and a free electron (or hole), if the solid material has shallow electron donors (or acceptors) that can be depopulated at a relatively low temperature, then the exchange can also occur at the same temperature. In short, the exchange is triggered by free electrons (or holes).

The difference in kinetics of thermal annealing of recoil damage and thermally activated isotopic exchange in the doped material arises due to the following reasons.[26,33] First, creation of additional donors and/or acceptors in the recoil track and, second, the density of bulk donors and/or acceptors can be affected by the concomitant γ radiation in the reactor and finally the chemical state and the site of the recoil species may

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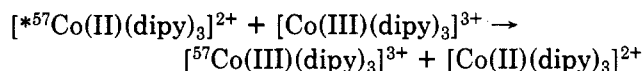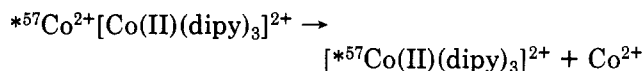(28) Thomas, V. G. *Radiochem. Radioanal. Lett.* **1972**, *12*, 97.
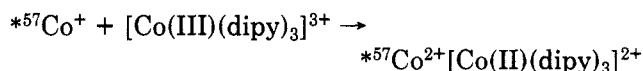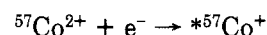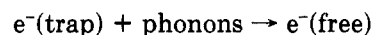(29) Kishore, K.; Venkateswarlu, K. S. *Radiochem. Radioanal. Lett.* **1973**, *13*, 17.
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differ from that of the dopant. According to our model, both the recoil species and the dopant undergo electronically excited isotopic exchange via interaction with an electron or hole. In some cases the thermal annealing is dominated by the bulk donors, and therefore the kinetics of isotopic exchange for the doped compound and the kinetics of thermal annealing are very similar, e.g., for tris(dipyridyl)cobalt(III) perchlorate.[36]

One may ask as to why one expects the free electrons or holes to excite dopants and why not the complex moiety? The dopant constitutes a defect site, while the nonbonding orbitals of the complex moiety form the conduction bond. We[37] exposed several cobalt complexes doped with $^{57}Co^{2+}$ to light of various wavelengths from a monochromator. For all the complexes, the maximum exchange occurred between 500 and 550 nm, which coincides with the absorption peak of Co^{2+}, while the main absorption peaks of these complexes lie in different regions. It seems that the photoinduced exchange is triggered by photoexcitation of the dopant, $^{57}Co^{2+}$, rather than the complex.

The "electronically excited exchange" model receives support from the comprehensive studies of Lazzarinis on the thermal annealing of ^{60}Co recoil atoms at anionic and cationic sites of neutron-irradiated crystals of double complexes[34,38-40] like cis-[Co(en)$_2$(NO$_2$)CNS]-[Co(edta)]·2H$_2$O. They reasoned that according to the "electronically excited exchange" model the annealing rate of the recoils would be governed by the rate at which electrons are thermally excited to the conduction band from donors, i.e., the activation energies associated with annealing and detrapping of electrons should be identical. The authors further reason that since the recoil atoms have a choice of exchanging with the cationic or anionic coordinated sites, the "electronically excited exchange" model predicts that the thermal annealing of the recoils in the cationic and anionic parts of Co(III) complexes must bear correlation with each other. Lazzarinis did observe this correlation; the isochronal annealing curves for anionic and cationic sites show the same number of steps occurring at the same temperatures. They also obtained a linear plot when the retention in the cation was plotted against retention in the anion, the slope measuring the ratio of the probabilities of exchange of the electronically excited recoil with the anionic and cationic sites.

Chappe et al.,[41] studied isochronal annealing and exchange in acetylacetonates of cobalt(III) and chromium(III). They observed that the same trapping levels were responsible for both the thermal annealing of the neutron-irradiated and thermally activated isotopic exchange in doped chelates. The influence of gases like oxygen was found to be analogous in both processes. The authors concluded that their observations support the "electronically excited" model involving detrapping

of holes from multidepth traps. One can rationalize practically all the existing data in the literature on the basis of the "electronically excited exchange" model.[33]

External Injection of Electrons and Holes

The basic premise of the "electronically excited exchange" model is the triggering of exchange by electrons or holes. So we decided to inject electrons or holes externally into cobalt phthalocyanine doped with $^{57}Co^{2+}$. In this material, the donors are rather deep and electrons can be detrapped only at relatively high temperatures.[42,43] Therefore, the effect of externally injected electrons or holes can be studied at room temperature without any perturbation from thermally detrapped electrons. Two different procedures were followed for injection of charge carriers. Electrons were injected from electrodes by space-charge-limited current technique.[43] Holes were injected by charge-transfer interactions between cobalt phthalocyanine and oxygen, iodine, or o-chloranil.[42]

Charge carriers can be injected into wide-band semiconductors, by appropriate choice of electrode material that makes ohmic contact (as opposed to blocking contact), and the observed current is limited by the space charge.[44,45] If the forbidden gap contains traps, either discrete or distributed quasi-continuously, then in the stationary state, the free carriers are in thermodynamical equilibrium with all the traps. The shape of the current vs. voltage plot is governed by the traps and their filling. The increase in the applied voltage results in the increase of the number of injected carriers and hence in raising the quasi-steady-state Fermi level toward the conduction band.

About 100 mg of α- or β-cobalt phthalocyanine was compacted into a 13-mm-diameter pellet (approximately 0.55 mm thick) in a die, with the help of a hydraulic press, in a glovebag with nitrogen flow. Gold or aluminum was coated on both sides of the pellet in a 5.5-mm-diameter circle. Charge carriers were injected by using space-charge-limited current (SCLC) technique, in an evacuated chamber. The voltage was increased steadily till it reached a value such that any further increase in the voltage could result in discharge in the material. We had subjected samples to these limiting voltages for several days. The ratio of the SCLC injection to the extrapolated ohmic current at the maximum potential used was approximately 10. From a variety of experiments,[43] we found that electrons were injected into cobalt phthocyanine (CoPc) pellets irrespective of whether one used Au or Al electrodes. The coated portion of the pellet was separated from the noncoated with the help of a scalpel. The two fractions were crushed well and aliquots were drawn from them for experiments. The CoPc powder was doped either before compaction or after the SCLC injection, using acetone solution of carrier-free $^{57}CoCl_2$. The uncoated material served as the reference material through which no electrons were injected. The unexchanged dopant,

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Table I
Space-Charge-Limited Electron Injection in Compacted
Pellets of Doped and Undoped Ball-Milled[a] α-Cobalt(II)
Phthalocyanine (Particle Size ~15 μm) and
Isotopic Exchange

material	incorp, %	
	after injection, %	thermal treatment, 1 h at 200 °C
doped CoPc		
coated fraction	12.5	21.5
reference	2.3	9.3
undoped CoPc		
coated fraction	1.3	21.2
reference	2.5	9.4

[a] The material was ball-milled in a glovebox with argon flow.

$^{57}Co^{2+}$, was chemically separated from the cobalt-57 activity incorporated in CoPc, through sulfuric acid precipitation.[42]

The SCLC-injected electrons either excite the $^{57}Co^{2+}$ dopant and induce exchange or get trapped. By direct interaction with injected electrons, $^{57}Co^{2+}$ undergoes exchange, raising the initial incorporation from 2.3% to 12.5% (Table I). Thermal treatment of the doped samples after electron injection yields incorporation of 21.5% in the coated fraction as compared to only 9.3% in the reference sample (i.e., the uncoated portion of the pellet through which electrons were not injected). These observations indicate that the injected electrons populate traps, which depopulate during thermal activation and induce further exchange.

The results are quite dramatic for the undoped pellets. After the SCLC injection, the coated and the noncoated portions were crushed and doped with $^{57}Co^{2+}$. After thermal treatment the incorporation in α-CoPc for the coated portion increased from 1.3% to 21.2%, while for the uncoated reference portion, the increase is from 2.5% to 9.4% (Table I). The latter is to be attributed to preexisting donors in the material. The population of donors is considerably enhanced after electron injection.

Physicorbed O_2 molecules on solid surfaces are known to act as electron traps[9,26,46] and would tend to inhibit isotopic exchange if it is triggered by detrapped electrons. On the other hand, oxygen is also known to form charge-transfer complexes with phthalocyanines.[47,48] Ysunaga et al.[47] have shown that O_2 can be made to diffuse into a single crystal of PbPc by thermal treatment for approximately 10 h above 230 °C. The dark conductivity at room temperature was observed to increase by 3 orders of magnitude. When the crystal was baked in vacuum, oxygen could be desorbed and complete reversibility was observed. Measurement of thermoelectric power indicated that positively charged carriers were generated by interaction with O_2. The authors concluded that the O_2 molecule acts as a center of carrier generation by accepting an electron from a neighboring PbPc molecule and releasing the holelike carrier. Raynor et al.[48] studied the charge-transfer in-

teractions between NiPc, ZnPc, and O_2 molecules using ESR spectroscopy. Baking the compounds under vacuum resulted in diminution of the ESR signal, but complete desorption was not observed. Our studies also show that oxygen is tenaciously adsorbed by CoPc and it is doubtful whether O_2 can be completely desorbed by baking in vacuum even at temperatures above 250 °C, when phase transformation occurs. We decided to carry out the preparations themselves in argon atmosphere and thereby avoided physisorption of O_2.

O_2 molecules diffuse into the α- and β-CoPc microcyrstallites and undergo charge-transfer interactions and inject holes in increasing concentrations with passage of time at any particular temperature. Our observations show that holes also induce exchange. For instance, aliquots of β-CoPc (particle size ~12 μm) that were heated in air at 200 °C for 1 h and 2 weeks and then doped with $^{57}CoCl_2$ showed 11.2% and 16.2% incorporation, respectively. If the size of the particles is relatively small and they are suspended in water, then one can inject a fairly large number of holes even at room temperature, through charge-transfer interactions. For instance, when β-CoPc was precipitated in finely subdivided form from sulfuric acid solution, exposed to air, the initial incorporation was observed to be as high as 25%. It seems that water assists diffusion of O_2 and due to its high dielectric constant enhances charge-transfer interactions between phthalocyanine and oxygen molecules.

The charge-transfer interactions of phthalocyanine with iodine and o-chloranil were studied by Kearns et al.[49,50] Aoyagi et al.[51] discuss the preparation of the phthalocyanine and iodine charge-transfer complex by diffusing iodine vapors in a single crystal of MgPc at 100–120 °C. Recently, Petersen et al.[52] prepared phthalocyanine iodine charge-transfer complexes by diffusion of vapor as mentioned above and also by heating iodine solution with suspension of phthalocyanine in chlorobenzene. These charge-transfer interactions are fairly strong, and the (hole) conductivity in phthalocyanine has been observed to increase several orders of magnitude.

We used both the above-mentioned procedures for preparing the CoPc–iodine complex. In some cases, the starting material was doped with $^{57}CoCl_2$ and in others doping was performed after the product was obtained. The incorporation generally rose from an initial value of about 1.5% to approximately 11%. However, the best results were obtained when the doped CoPc was mixed thoroughly with 2 equiv of iodine powder or o-chloranil and compacted into a pellet, incorporations of 23.4% and 30%, respectively, being obtained. The charge-transfer interactions of CoPc with iodine and o-chloranil are much stronger than with oxygen, as is evident from the larger magnitudes of exchange resulting from a larger concentration of injected holes and also from the observation that the magnitude of exchange is practically independent of the particle size

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Healing of Damaged Molecules

Table II
Particle Size and Nonequilibrium Concentrations of Electrons and Holes

material	magnitude of exchange induced by holes (air-heated sample, doped), %	magnitude of exchange induced by detrapped electrons (doped sample heated in vacuum), %	sum of I and II, %	magnitude of exchange induced by electrons and holes concurrently (doped sample heated in air), %
	I	II		
α-CoPc, manually crushed (~57 μm); 24 h at 250 °C	6.3	10.7	17.0	12.5
α-CoPc, ball-milled in Ar (~11 μm); 24 h at 250 °C	11.1	10.4	21.5	22.5
α-CoPc (~57 μm), treated with iodine; 24 h at 200 °C	4.7	10	14.7	15.5

(unlike the exchange induced by thermal treatment in oxygen).

Particle Size and Nonequilibrium Concentrations of Electrons and Holes

We would now consider the relation between particle size and the relative contribution of electrons and holes toward isotopic exchange. The magnitude of exchange observed by heating the undoped material in air and then doping it is determined by the concentration of injected holes through charge-transfer interactions between oxygen and phthalocyanine molecules. On the other hand, the magnitude of exchange observed after thermal treatment of an evacuated doped sample is governed by the concentration of detrapped electrons. The magnitude of exchange induced independently by holes and electrons for a specified temperature are given in Table II. If the thermal treatment of a doped sample is carried out in air, we would have both detrapped electrons and injected holes. One would expect considerable recombination of electrons and holes, and the product of their concentrations would tend toward the equilibrium value characteristic of the material at the specified temperature (this is analogous to the product of H^+ and OH^- concentrations in aqueous solutions). In view of this recombination, the total magnitude of exchange observed for doped material heated in air shoud be considerably less than the sum of magnitudes of exchange induced independently by holes and electrons at any specified temperature.

This conclusion is borne out by observations at different temperatures for samples of α-CoPc and β-CoPc having coarser particle subdivision (>20 μm). For instance, let us compare the exchange observed for the manually crushed α-CoPc (particle size, ca. 57 μm) at 250 °C for 24 h under different conditions (Table II). When the air-heated sample was doped, 6.3% units exchange was induced by holes, while for the doped sample heated in vacuum, 10.7% units exchange was induced by detrapped electrons. The magnitude of exchange induced by electrons and holes concurrently during thermal treatment of the doped material in air was 12.5%, which is considerably less than the sum of the exchange induced by electrons and holes independently, viz., 17.0% (Table II). However, one observes a dramatic change in the behavior of the finely subdivided ball-milled samples (particle size, ca. 11 μm); the magnitude of the total exchange for doped samples heated in air is quite close to the sum of the magnitudes of exchange induced independently by holes and elec-

trons, one at a time (Table II).

This behavior is amazing and is indicative of the fact that the relaxation time for electrons and holes has been enhanced dramatically. It seems that the deep electron donors that act as recombination centers are inactivated when large concentrations of holes swamp them. After the electrons in the deep traps are annihilated, they are occupied by holes and it seems that the site undergoes stereodistortion so that it becomes less accessible to an electron. In short, the efficacy of recombination centers is very poor once they are occupied by holes. It is apparent from these observations that O_2 is effective in populating a large fraction of recombination centers with holes in finely subdivided particles (ca. 11 μm). On the other hand, in coarser particles the large majority of recombination centers remain unpopulated by holes and still maintain their efficacy as recombination centers.

To substantiate this idea, we treated the manually crushed α-CoPc (coarse particles, ca. 57 μm) with iodine, compacted it into a pellet, left it standing for several hours, and then manually crushed the pellet and distilled off iodine under dynamic vacuum at ca. 10 °C. The coarse material after this treatment behaves like finely subdivided materials[53] (Table II). Iodine and phthalocyanine undergo stronger charge-transfer interactions as compared to oxygen, and a larger concentration of holes would be injected and moreover their mean free path is also likely to be longer. Hence, even in coarser particles, the bulk of the recombination centers are incapacitated, and the detrapped electrons are quite effective in inducing isotopic exchange even in the presence of a large concentration of holes. Under these conditions, the concentrations of electrons and holes are very much larger than that of the equilibrium state. A simple physical picture describing the above behavior could be as followed: a neutral cobalt phthalocyanine molecule defect site may trap a hole and become positively charged. The molecule may undergo a stereodeformation and not allow any easy transfer of an electron from its neighbors. In this fashion, the recombination center can become deactivated.

Concluding Remarks

Isotopic exchange was initially observed in the systems $Ca(IO_3)_2$ doped with $^{131}I^-$ and K_2CrO_4 doped with $^{51}Cr^{3+}$ at relatively high temperatures. Later, we found that considerable isotopic exchange could occur in some

(53) Kalliat, M.; Nath, A., unpublished work.

metal complexes even at room temperature, e.g., in tris(dipyridyl)cobalt(III) perchlorate doped with $^{57}Co^{2+}$. This is a very intriguing observation, as the isotopic exchange involves high activation energies associated with breaking of strong coordination bonds. We proposed that the large activation barrier for exchange is surmounted by the electronic excitation of the dopant resulting from its combination with a free electron or hole. The highly electronically excited radiodopant interacts with a neighboring coordinated moiety, and the ligands are transferred onto the dopant. The material can have shallow electron donors (or acceptors) that can depopulate and trigger exchange at relatively low temperatures.

We have verified the basic feature of the proposed model by direct injection of electrons and holes into cobalt phthalocyanine doped with $^{57}Co^{2+}$. Both the injected electrons and holes lead to considerable exchange. These technqiues may be applied to labeling complex biomolecules like vitamin B_{12}. At present vitamin B_{12} is labeled biosynthetically and it involves tedious purification procedures.

Free electrons and holes can trigger fairly energetic reactions, and their role in biological systems, like the photosynthetic apparatus, can perhaps be evaluated via space-charge-limited injection of electrons and holes. These studies may also help in verifying some of the proposed steps in the primary process.

The radiodopant can also serve as a probe and provide useful information regardng the electronic behavior of the material. For instance, studies on $^{57}Co^{2+}$-doped cobalt phthalocyanine system indicate that the recombination centers in CoPc can be deactivated by interaction with holes. Subsequently, if both electrons and holes are injected simultaneously, then they seem to coexist for considerable lengths of time without recombinations and that the free electron or hole can interact with a dopant, $^{57}Co^{2+}$ ion, and induce isotopic exchange. It seems that the spatial distortion of $CoPc^+$ molecules (trapped holes) hinders the transfer of electron into the site and thereby reduce dramatically the rate of electron-hole recombination. Materials endowed with this unusual property are likely to find applications in photocatalysis and as electrode material in solar photoelectrochemical cells, where recombination of charge carriers often limits the efficiency.

Quantum Yield Variation over Narrow Spectral Regions in Coordination Photochemistry

Cooper H. Langford

Department of Chemistry and Canadian Picosecond Flash Photolysis Centre, Concordia University, Montreal, Quebec, Canada H3G-1M8

In the visible and near-UV region of the spectrum, most organic molecules offer a limited number of distinct excited states. To examine competition among a rich variety of organic photochemical pathways, it is necessary to work with far-UV sources. When this is done, significant reactivity differences over *narrow spectral regions* can be observed, although it is still called "unusual" wavelength dependence.[1] Transition-metal complexes,[2] on the other hand, commonly possess both ligand field and charge-transfer excited states in the visible and near-UV region of the spectrum and commonly several of both! For example, the lower energy spectrum of a simple chloropentaamminecobalt(III) complex ion displays chloride to metal charge transfer with both a singlet and triplet excited state, four ligand field levels derived from the strong field d^6 configuration each of which yields singlet and triplet states, and quite probably an accessible quintet state related to the weak field d^6 configuration. It should not be surprising that plausible evidence for the involvement of four distinct states in the photochemistry of this compound can now be adduced from wavelength dependence of yields.

However, it is not the point of this Account to complicate photochemistry with a taxonomy of exotic "photofauna". In nature two major photoreactions, photosynthesis and vision, seem to suggest a common lesson. Productive exploitation of photons can be based on a very rapid "irreversible" photochemical reaction that competes with facile relaxation to a lower, longer lived, excited state. This latter state seems less useful (perhaps because the system has already dissipated too much energy). I am thinking, of course, of the chlorophyll singlet vs. its triplet and the picosecond changes in the Raman spectra of visual pigments. To understand the strategy of such photon exploitation, it is necessary to discover the factors that govern competition among pathways in the short time domain. The simplest approach is to look for measurable variations of photochemical and photophysical yields *over narrow frequency domains*. Such experiments are quite practicable in the dye laser era, and transition-metal com-

Cooper H. Langford received an A.B. from Harvard in 1956 and a Ph.D. from Northwestern in 1960. After a postdoctoral period at University College London he has taught at Amherst, Carleton University (Ottawa), and most recently has become Professor and Chairman of Chemistry at Concordia University in Montreal where the Canadian Centre for Picosecond Flash Photolysis is under development. His research interests have included ligand substitution processes, solvent effects in kinetics of metal complexes, photochemistry using laser excitation sources, and interaction of transition-metal ions with naturally occurring organic ligands.

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