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Isotopic Exchange Reactions in Solids

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Solid state exchange has been investigated in $Fe(H_2O)_6[FeEDTA \cdot H_2O]_3 \cdot H_2O$, $[Co(NH_3)_5Cl]Cl_2$ *and* $Cr(H_2O)_6 \cdot Cr(C_2O_4)_3$. *Each of these systems shows different kinetic characteristics. The iron complex resembles the analogous cobalt complex, but exchange is more easily distinguished from decomposition. The exchange of chlorine in the cobalt pentammine complex shows new characteristics. Different samples give widely different energies of activation but the exchange is not affected by crushing or irradiation of the material. In the chromium complex isomerisation can occur on heating.*

Introduction

Several more solids in which isotopic exchange of atoms might be studied have been investigated. Some compounds could not be prepared, dissolved and the two forms of the element separated without substantially complete isotopic exchange. Hydrated mercury(II) ethylenediamine tetra-acetato mercurate(II) was in this category. Specifically labelled mercury(II) tetracyanomercurate(II) could not be made. In others, specific labelling was possible but no thermal exchange could be detected below the decomposition temperature of the solid. Iron(II) pentacyanonitrosylferrate, $Fe[Fe(CN)_5NO]xH_2O$ belongs to this group. Three compounds proved suitable for more detailed investigation and the results are reported in this paper.

A. Cation–Complex Anion Exchange in $Fe(H_2O)_6[FeEDTAH_2O]_3 \cdot H_2O$

Exchange has been reported in the related solid cobalt complex $Co(H_2O)_6[CoEDTA]_2 \cdot 4H_2O$ [1, 2], following heating after gamma irradiation, but in this compound the two cobalt atoms are in different oxidation states. Further it is very difficult to distinguish the exchange from thermal decomposition, which takes place at only a slightly higher temperature. Since the exchange in the iron complex might be followed *in situ* by Mössbauer spectroscopy, using ^{57}Fe labelling, it appeared interesting to explore the exchange in the iron compound using a radioactive tracer technique first. It is known that iron(III) only exchanges very slowly with $[FeEDTAH_2O]^-$ in solution [3].

Experimental

Preparation of labelled $Fe(H_2O)_6[FeEDTAH_2O]_3 \cdot H_2O$

The preparation of the complex acid $H[FeEDTAH_2O]$ has been described by Lambert *et al.* [4]. The iron(III) salt has been reported by Kennard [5], but the method of preparation used was unsuitable for specific labelling.

Specifically labelled material was prepared by exchanging the complex anion onto an Amberlite IRA-401 column (27 cm long, 2 cm i.d.) in the Cl^- form using B.D.H. $Na[FeEDTAH_2O]$. After washing with water, the column was eluted by iron(III) nitrate solution, using the required amount to form the iron(III) salt of the complex anion. All operations were conducted with cold solutions. The eluate was freeze dried. The solutions and the column were protected from light using aluminium foil wrappings to avoid photodecomposition [3]. Using ^{59}Fe labelled iron(III) nitrate the complex specifically labelled in the cation could easily be prepared. Most of the data were obtained with such material but one measurement was made using anionically labelled material prepared in an analogous manner, using ^{59}Fe labelled $H[FeEDTAH_2O]$ prepared by the method described by Lambert *et al.* [4].

The products were analysed for Fe, C, H and N and the results were in close agreement with the requirements of the above formula.

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Separation procedure

Since the exchange is very slow in acid solutions [3], the separation of the cationic and anionic iron was made by ion exchange, using the cation exchange resin Amberlite IR-120 in the H$^+$ form. A sample of 50 mg of the complex was dissolved to give 25 cm^3 of solution and the solution shaken with 10 cm^3 of the resin. When no further change in the colour of the aqueous phase took place the resin was separated and washed. The solution and washings were combined, made up 100 cm^3 and used to measure the activity of anionic iron. The cationic activity was obtained by difference using the total activity measured on a solution of the original complex. The method was checked by analytical determination of the iron content of the anionic fraction.

The zero time exchange is given by 4/3 α_0^a/α_0 for cationically labelled material, where α_0^a is the zero time anionic activity and α_0 the total activity.

Measurements of the zero time exchange immediately after preparations made with cold solutions gave values around 6%, sufficiently low for investigation of the solid state exchange. No exchange occurred at room temperature.

Activity measurements

These were made on the solutions using an annular liquid cell Geiger counter.

Thermal stability of the complex

A thermogravimetric analysis at 5°/min in a stream of nitrogen showed the complex steadily lost water from 300 to 393 K, by which temperature only one molecule of water remained, probably that in the complex anion. Between 393 and 413 K the weight was constant. A spectrophotometric examination of the effect of heating for 2.25 h periods between 393 and 423 K, using the $[\mathrm{FeEDTAH_2O}]^-$ absorption at 256 mμ, showed no decomposition at 393 K, 1.9% at 403 K, 3.1% at 413 K, and 26.0% at 423 K. Exchange measurements were therefore concentrated on temperatures below 413 K.

Exchange treatments

Samples of the complex were sealed in small glass ampoules in air and heated in a thermostaticly controlled electric oven (±1 K). Gamma irradiated samples were irradiated at room temperature at a dose rate of 0.72 kGy h^{-1}. The fraction remaining to exchange, F, is given for cationically labelled material, measuring the anionic activity, by $F = (3 - 4\alpha)/(3 - 4\alpha_0)$, where α = fraction of the total activity in the anionic species at time t, and α_0 the corresponding fraction at zero time.

Results

As is commonly the case in these systems although the behaviour of a given preparation is reproducible, that of different preparations is not (Fig. 1). It was verified that exchange can be followed from cation to anion and *vice-versa*. All subsequent sets of data were obtained each using material from a single preparation.

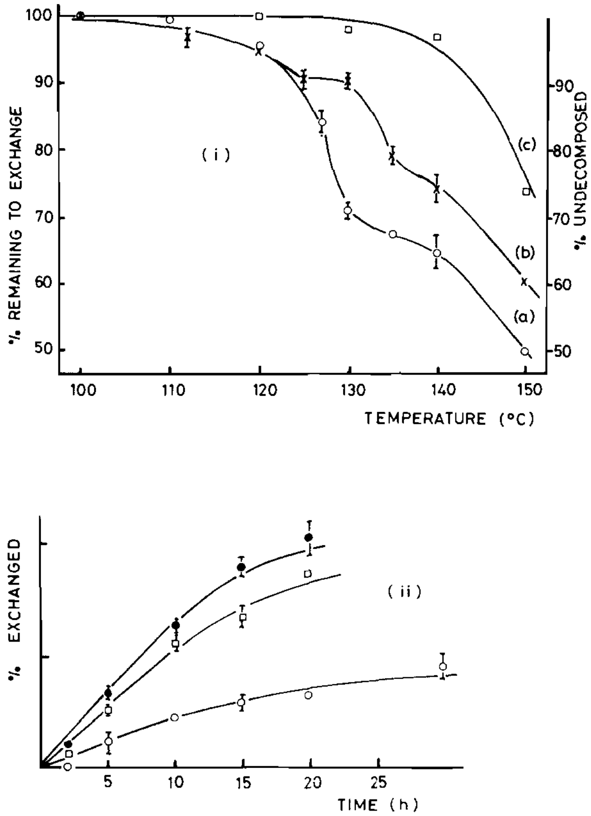

Fig. 1. (i) Exchange isochronal for $^{59}\mathrm{Fe(H_2O)_6[FeEDTA\cdot H_2O]_3H_2O}$. Time 135 minutes. ○ Sample A, × Sample B: Left hand ordinates. □ Thermal Decomposition: Right hand originates. (ii) Exchange isothermals for $^{59}\mathrm{Fe(H_2O)_6[FeEDTA\cdot H_2O]_3H_2O}$. ○ 373 K, □ 383 K, ● 393 K.

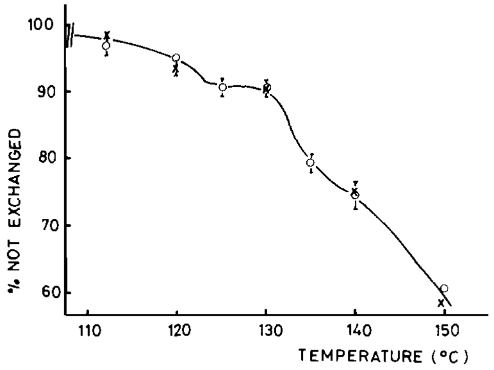

Fig. 2. Exchange isochronal for $^{59}\mathrm{Fe(H_2O)_6[FeEDTA\cdot H_2O]_3H_2O}$. Sample B. Time 135 minutes. × γ Irradiated sample, ○ Untreated sample.

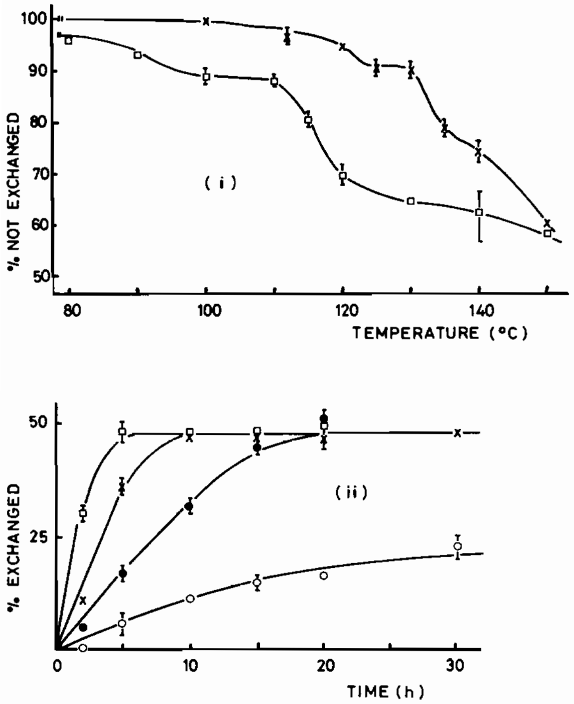

Fig. 3. (i) Exchange isochronal for $^{59}Fe(H_2O)_6[FeEDTA\cdot H_2O]3H_2O$. Sample B. Time 135 minutes. □ Crushed material, × Untreated material. (ii) Exchange isothermals for $^{59}Fe(H_2O)_6[FeEDTA\cdot H_2O]3H_2O$. Sample B. □ 393 K Crushed, ● 393 K Untreated, × 374 K Crushed, ○ 373 K Untreated.

A dose of 50 kGy was without effect on the exchange (Fig. 2). A spectrophotometric check showed no appreciable radiolytic decomposition had occurred.

However, as is seen in Fig. 3, crushing the crystals of the complex considerably accelerated the exchange.

To investigate the effect of the dehydration which may accompany the above thermal treatments a comparison was made with a sample that had been dehydrated by heating to 368 K while pumping. This dehydration did not produce any appreciable immediate exchange. In addition some samples of the same original complex were heated in open tubes. The results are shown in Fig. 4.

B. Ligand–Anion Exchange, $[Co(NH_3)_5Cl]Cl_2$ System

The first experiments involving the exchange of atoms in a solid matrix were of this type. Schmidt and Herr [6] found but little exchange with the bromo pentammine complexes of rhodium and iridium, but with the dihalo-bis ethylene-diamine cobalt complexes Schmidt and Rössler found that exchange of halide atom could occur with the halo-anion rather easily [7]. They also noted that irradiation of the labelled complex with ionising radiation facilitated a subsequent thermally initiated exchange, although its immediate effect was negligible. They did not report any abnormality of the exchange kinetics. The thermal stability of chloropentammine cobalt-(III) chloride suggested its suitability for such a study. Biltz [8] and, more recently, Wendlandt [9] agree that no loss of ammonia and coordination of additional chloride occurs below 453 K. The system is also attractive because a simple mechanism would seem at least possible.

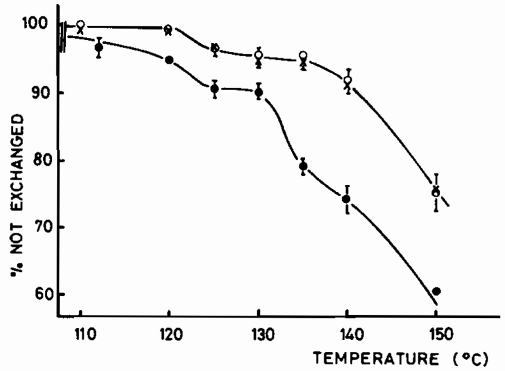

Fig. 4. Exchange isochronals for hydrated and partially dehydrated $^{59}Fe(H_2O)_6\cdot[FeEDTA\cdot H_2O]3H_2O$. Sample B, time 135 minutes. ○ Dehydrated material, × Untreated open tubes, ● Untreated sealed tubes.

Experimental

Preparation of labelled $[Co(NH_3)_5Cl]Cl_2$

Chloropentammine Co(III) chloride was prepared via carbonato pentammine Co(III) nitrate as described by Basolo and Murmann [10].

(a) Anionically labelled material. The chloride in a solution containing 1.0 MBq of ^{36}Cl was exchanged onto a small column of Amberlite IRA-400 (15 cm × 1 cm). A solution of 2.5 g of the chloropentammine Co(III) chloride in 500 cm^3 of water was passed through the column. The eluate was partly freeze dried and partly vacuum concentrated and then allowed to crystallise (this method is based on a procedure used by Peters and Fiore [11]). Two preparations made in this way are distinguished as A and B, respectively.

(b) Cationically labelled. Carbonatopentammine Co(III) nitrate, prepared as before, was treated with 2 *M* perchloric acid. On evaporation $[Co(NH_3)_5H_2O](ClO_4)_3$ was obtained. Addition of concentrated hydrochloric acid to a saturated solution of the perchlorate precipitated $[Co(NH_3)_5H_2O]Cl_3$. A solution

of 3 g of the $[Co(NH_3)_5H_2O]Cl_3$ in the minimum volume of water at 353 K was treated with 0.73 MBq of the carrier free ^{36}Cl chloride solution and the mixture digested for four hours at 353 K. After cooling $[Co(NH_3)_5Cl]Cl_2$ was precipitated by addition of 0.1 dm^3 of concentrated hydrochloric acid at 273 K. Solution and reprecipitation of the salt was continued until the anionic chloride had a negligible activity [12]. Both samples were analysed for cobalt, chloride and nitrogen and the results were the same as the calculated composition within the experimental error.

A thermogravimetric analysis confirmed that no thermal decomposition (weight loss) took place below 447 K.

Separation procedure

Archer *et al.* [13] have shown that the half life for aquation of $[Co(NH_3)_5Cl]^{2+}$ at 298–308 K is about 100 h, so that a reasonably rapid separation of Cl^- and $[Co(NH_3)_5Cl]^{2+}$ in aqueous solution should encounter no inaccuracy from this process.

Samples of 25 mg of the $[Co(NH_3)_5Cl]Cl_2$ were dissolved in 25 cm^3 of cold water. An aliquot of 10 cm^3 was used for the measurement of the total activity. The remaining 15 cm^3 was shaken with 10 cm^3 of the cation exchanger, Amberlite IR-120 H in the acid form. After a few minutes, when the solution became colourless, the aqueous phase was separated. The resin was washed and the washings combined with the original aqueous phase for measurement of the anionic activity. The efficiency of the separation was checked by conventional analysis, it was more than 99.5% efficient. The cationic activity was obtained by difference.

Activity measurements

All measurements on the purely β active ^{36}Cl were made on aqueous solutions using an annular Geiger counter. The long life of ^{36}Cl precludes decay corrections and the solutions measured were of sufficiently constant density to preclude corrections on that account.

Exchange treatments

a. Thermal. As in section A. b. Ionising irradiation. As in section A. In both cases, the samples were contained in sealed glass tubes in the presence of air.

Results

Zero time exchange

The initial preparations always showed some exchange. The zero time exchange, E_o, is given by $3/2\ \alpha_o^a/\alpha_o$, where α_o^a is the initial anionic activity of cationically labelled material and a_o is the total activity, or $(3 - 3\ \alpha_o^a/\alpha_o)$ for anionically labelled material. It was found E_o (sample A) = 10.3 ± 0.8%, E_o (sample B) = 2.0 ± 0.9% and E_o = 0.1 ± 0.5% for cationically labelled material.

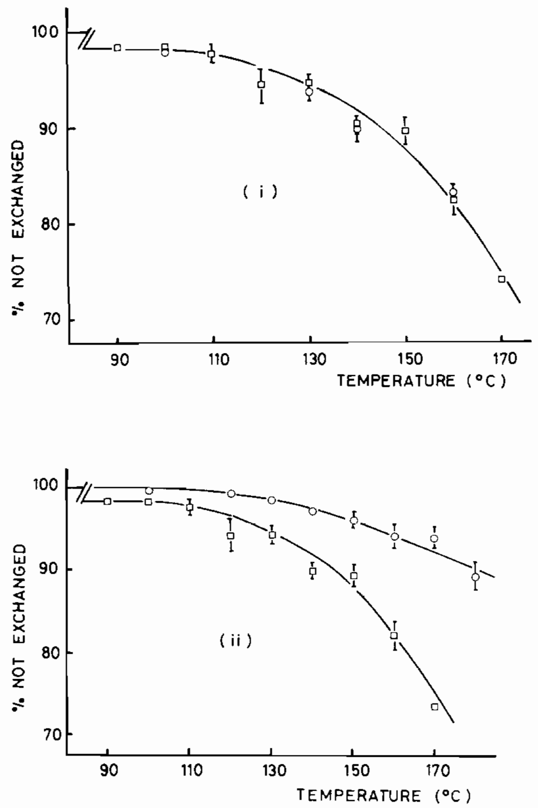

Fig. 5. (i) Exchange isochronals for $[Co(NH_3)_5Cl]\ ^{36}Cl_2$. □ Untreated, ○ γ irradiated (10^4 Gy). (ii) Exchange isochronals for $[Co(NH_3)_5Cl]\ ^{36}Cl_2$. ○ Sample A, □ Sample B. Time 70 minutes.

Exchange isochronal

A heating of 4200 s was chosen. The values are generally the mean of three observations and the reproducibility for material from a given batch of labelled material was ±1.4% in the fraction unexchanged, F.

$$F = (2 - 3\ \alpha_t^a/\alpha_o)/(2 - 3\ \alpha_o^a/\alpha_o) = (2 - 3\alpha)/(2 - 3\alpha_o).$$

Figure 5 (curve A) shows the isochronal for sample A of the anionically labelled material. A portion of this material was irradiated to a total dose of 100 kGy. The irradiation did not produce any appreciable decomposition of the compound. The irradiation did not lead to additional exchange nor did it influence the subsequent thermal annealing (Fig. 5).

The material identified as sample B consisted of much larger crystallites than sample A. The iso-

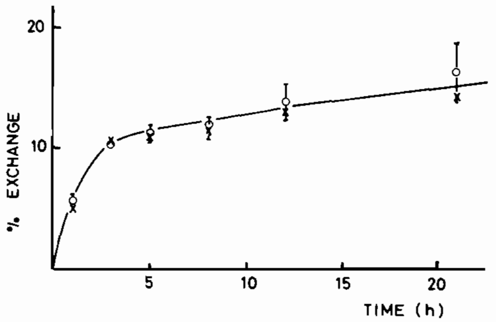

Fig. 6. Exchange isochronals for $[Co(NH_3)_5Cl]\,^{36}Cl_2$. Sample B, time 70 minutes. X Crushed sample, o Untreated sample.

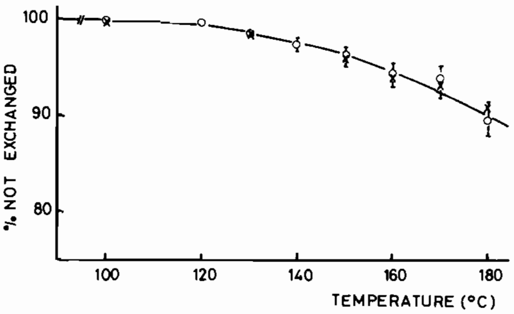

Fig. 7. Exchange isothermals at 433 K. o $[Co(NH_3)_5Cl]\,^{36}Cl_2$, X $[Co(NH_3)_5\,^{36}Cl]Cl_2$.

chronal for the same period of heating is shown in curve B. Fig. 5 (ii).

Different preparations also gave materials yielding different isochronals, although the reproducibility of measurements on the same batch of compound was good.

Simply crushing the crystals of a preparation similar to that of sample B did not appear to alter the exchange isochronal, although the size of crystallites become similar to that of sample A. The data are shown in Fig. 6.

The true exchange character of the reaction was demonstrated by comparing the isothermal reactions of samples labelled anionically and cationically. All the data fell on the same curve. Figure 7 shows the isothermal obtained for the two samples. It will be noted that this exchange, like other solid state exchange and annealing reactions, does not follow the kinetics of a single first-order process.

C. Chromium Exchange in $Cr(H_2O)_6 \cdot Cr(C_2O_4)_3$

Chromium(III) tris-oxalato chromate(III) seemed an interesting system to explore since it might be possible to find evidence of the exchange mechanism because the isomeric compound $Cr(H_2O)_4Ox \cdot CrOx_2(H_2O)_2$ ($Ox \equiv C_2O_4$) is also known [14, 15]. The specifically labelled compound can be made and exchange of chromium between the cationic and anionic forms is slow in aqueous solution [15].

Since $CrOx_3^{3-}$ can be resolved into d and l forms it is unlikely that exchange of anionic and cationic chromium will be fast in aqueous solution.

Experimental

Preparation of specifically labelled $Cr(H_2O)_6$-$CrOx_3$

The preparation has to avoid aquation of the $CrOx_3^{3-}$. A cold solution of $K_3CrOx_33H_2O$, prepared as described by Booth [16], was anion exchanged with Amberlite IRA-401 in the chloride form. (A similar column to that mentioned in A.) The column was then eluted with the requisite amount of a strong solution of chromium(III) perchlorate. The eluate was immediately freeze dried to give fine blue crystals. Attempts to prepare the compound using the method of Douville *et al.* [17] always gave the isomeric $Cr(H_2O)_4Ox \cdot CrOx_2(H_2O)_2$. Using the above method with cationically labelled chromium with ^{51}Cr gave the specificly labelled product. The product was stored in a closed bottle at solid CO_2 temperature.

Analysis

The chromium, carbon and hydrogen contents of the product were in good agreement with the formula. But this would also be the case for a mixture of the isomers. The anionic and cationic components were therefore separated by ion exchange and analysed separately [18]. The oxalate and chromium contents of the anionic fraction, determined volumetrically, indicated about 8% of $Cr(H_2O)_4Ox \cdot CrOx_2(H_2O)_2$. Elution of the column with 0.05 *M* perchloric acid removed the $Cr(H_2O)_4Ox^+$ and titration of the oxalate in the eluate confirmed the extent of isomerisation.

A sample of cationically labelled $Cr(H_2O)_4Ox \cdot CrOx_2(H_2O)_2$ was prepared. Inactive $Cr(H_2O)_4Ox \cdot CrOx_2(H_2O)_2$ was made by dissolving freshly precipitated chromic hydroxide in oxalic acid solution. The product was separated by freeze-drying. A solution was then contacted with a cationic resin containing ^{51}Cr labelled $Cr(H_2O)_6^{3+}$. After removing the resin cationically labelled $Cr(H_2O)_4Ox \cdot CrOx_2(H_2O)_2$ was recovered by freeze drying. Ion exchange separation of anionic and cationic components confirmed the identity and purity of the product.

Separation procedure

The samples were dissolved and anionic and cationic components separated by removing the cations on Zerolit-225(H). After washing, the com-

TABLE I. 2 h Treatments.

Temp/K	% $Cr(H_2O)_4Ox$ formed in $Cr(H_2O)_6 \cdot CrOx_3$	% Exchange in $Cr(H_2O)_6 \cdot CrOx_3$	% Exchange in $Cr(H_2O)_4Ox \cdot CrOx_2(H_2O)_2$
20	11.6	1.8	
32	11.8	1.8	4.0
50	12.7	6.8	11.0
64	12.7	9.3	33.4
74	29.1	15.8	60.8
90	30.4	20.5	78.8
100	35.4	44.5	95.1
110	74.2	92.3	

bined aqueous phases were made up to a fixed volume.

Activity measurements

The activities were measured on aliquots in an annular Geiger–Müller counter.

Exchange Treatments

Thermal annealing was conducted as for A and B.

Results

The zero time exchange values for the preparations were

$Cr(H_2O)_6 \cdot CrOx_3$ 8–9%

$Cr(H_2O)_4Ox \cdot CrOx_2(H_2O) \sim 14\%$

It was quickly found that exchange takes place above about 303 K. But the colour of the samples changed and at the higher temperatures they lost some water unless sealed tubes were used. An examination using the separation procedure already outlined showed that on heating solid $Cr(H_2O)_6 \cdot CrOx_3$ there is formation of $Cr(H_2O)_4Ox \cdot CrOx_2(H_2O)_2$ and that small amounts of $Cr(H_2O)_6CrOx_3$ form on heating $Cr(H_2O)_4Ox \cdot CrOx_2(H_2O)_2$.

A series of isochronal measurements were then made on $^{51}Cr(H_2O)_6CrOx_3$ and $^{51}Cr(H_2O)_4Ox \cdot CrOx_2(H_2O)_2$ measuring the transfer of activity from cationic to anionic chromium and, for the $^{51}Cr(H_2O)_6CrOx_3$, the amount of $^{51}Cr(H_2O)Ox \cdot CrOx_2(H_2O)_2$ formed. The data are shown in Table I.

Discussion

A) The exchange in the iron EDTA complex is more easily distinguished from the decomposition of the complex (Fig. 1) than is the case for the cobalt complex [2]. It will be noted that the experiments yielding the data in Fig.1 were conducted with cationically labelled material so that the exchange is proceeding in the opposite direction to the gross decomposition. Further the exchange can only be explored in the cobalt complex using the partially radiolysed material. The iron complex appears to be more resistant to radiolysis and indeed ionising irradiation is without effect on the subsequent thermal exchange (Fig. 2). Crushing the crystallites, however, considerably modifies the course of the exchange process (Fig. 3).

Like the cobalt complex exchange takes place less easily in the dehydrated than in the hydrated material, Fig. 4. A thermogravimetric examination shows that heating in an open system leads to loss of water so that samples heated in open tubes behaved like the dehydrated material.

As has been shown in a previous paper, the steps seen in the isochronal curves are too steep to be explained on the basis of a number of exchange channels with different E_{act} and/or frequency factors [19]. Rather high E_{act} and altogether improbably large frequency factors would be needed. Taking into account the difference between the hydrated and dehydrated material it seems likely that the exchange is a discontinuous process associated with the water vapour–hydrated salt equilibrium in the sealed tubes. This conclusion is compatible with the enhanced exchange with the crushed material. The process may be like that described for the $Ni(H_2O)_2 \cdot Ni(CN)_4 \cdot 4H_2O$ system [19].

B) The exchange in this system shows quite different characteristics from A. The absence of any appreciable effect of both crushing and ionising irradiation, Figs. 5 and 6, suggests that the exchange is not much affected by the specific surface of the crystallites; nor by dislocations. In this respect the system is different from all those so far examined [1, 2, 19–21]. However, the behaviour of different preparations of apparently chemically identical products varies considerably, Fig. 5. This suggests that the process may proceed via a small concentration of ligand deficient species, as proposed by Rössler *et al.* [22] in a slightly different situation. If this is the case, we must suppose that the concentration of ligand deficient entities is not much affected by crystalline size, crushing or ionising irradiation, but is sensitive to some other detail of the preparation.

Like many similar kinetic analyses of processes going on in solids, the best fit is obtained with a rather high frequency factor. This peculiarity can be relaxed somewhat if one accepts different frequency factors for the different exchange channels. As usual the reliability of the lowest E_{act} is greater, the highest E_{act} being sensitive to the long time points on the exchange isotherms. Previous experience with related processes in solids suggests that these points may be anomalous, possibly because the frequency factor may change during the heating.

The mathematically best fit for both samples for which extensive data were obtained, required a frequency factor of 10^{15}. But fits within the experimental error were obtained with 10^{13}. For sample A, three energies of activation, 1.15, 1.34 and 1.52 eV, with proportions 1.7%, 7.9% and 90.4%, respectively, exchanging by these channels. For sample B, the energies were 1.30, 1.46 and 1.75 eV with proportions of 1.8%, 11.0% and 87.2%.

It is noteworthy that in this system for the greater part of the material but a single exchange channel seems possible and that changes in the energies of activation, rather than in the proportions of lattice inhabitants for which a given exchange channel is open, account for the differences between different preparations (contrast 19 and 21).

C) The chromium oxalate complex system is complicated by the solid state isomerisation. This isomerisation has not been reported previously, although Malati *et al.* [23] have investigated the solid state *cis–trans* isomerisation in $KCrOx_2(H_2O)_2$. In these circumstances, a detailed kinetic analysis does not seem warranted, but the data in the table do tend to confirm the hypothesis that exchange in this solid proceeds by ligand transfer.

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