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Deuteration Reaction of Malonate Hydrogens in Some Monomalonatocobalt(III) Compounds[1)]

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The rate of deuteration at malonate hydrogens has been measured for $[Co(mal)(N)_4]^+$ and $[Co(malH)(NH_3)_5]^{2+}$ ions in aqueous solution over the pD range of 2 to 8, where mal=malonate dianion, malH=malonate monoanion, and $(N)_4=(NH_3)_4$, (ethylenediamine)$_2$, (1,3-propanediamine)$_2$, (1,10-phenanthroline)$_2$, or (2,2′-bipyridine)$_2$. For the tetraamine type complexes with a chelated malonate ligand, the deuteration process is acid-catalysed up to pD=about 4 and base-catalysed at higher pD values. This contrasts with the behavior of the unidentate malonate ligand, for which the deuteration is base-catalysed up to pD=3.5, whereupon the deprotonation of the carboxylate group takes place and the deuteration rate steps down to a constant, pH-independent value. The deuteration mechanisms are discussed.

In 1967, Yoneda and Morimoto[2)] found that the methylene hydrogens of malonate chelated to a cobalt (III) ion exchange with deuterium in deuterium oxide. Since the exchange was observed simply by dissolving the cobalt(III) compounds in deuterium oxide, this facile exchange was ascribed to the electron-withdrawing power of the central metal ion. Subsequently, a similar facile deuteration was confirmed to take place for several malonatocobalt(III) complexes.[3–7)] Buckingham *et al.* noted that the malonate hydrogens in $[Co(mal)_2(en)]^-$ and $[Co(mal)(en)_2]^+$ ions[4)] appear to undergo acid-catalysed and probably base-catalysed exchange. Farago and coworkers[5–7)] recently measured the deuteration rates for $[Co(mal)(bpy)_2]^+$, $[Co(mal)_2(en)]^-$, and $[Co(mal)(en)_2]^+$ in the pD range of about 2 to 3 at several temperatures. They confirmed that the exchange reaction is in fact acid-catalysed. We have measured the exchange rates at 36.4 °C over a wide pH region for $[Co(mal)(N)_4]^+$ type of complexes, as well as $[Co(malH)(NH_3)_5]^{2+}$, where $(N)_4$ represents $(NH_3)_4$, $(en)_2$, $(tn)_2$, $(phen)_2$, or $(bpy)_2$.

Experimental

Materials. Deuterium oxide (99.8 atom% D minimum) was obtained from E. Merck (Darmstadt). Malonic acid and other chemicals were purchased from Katayama Chemical Industries Co., Ltd. (Osaka).

Pentaamminemalonatocobalt(III) perchlorate,[8)] tetraamminemalonatocobalt(III) perchlorate,[9)] and bis(ethylenediamine)malonatocobalt(III) iodide hemihydrate,[10)] were prepared by the literature methods and the identity was confirmed by visible absorption and NMR spectra. The en compound was optically resolved by (−)-$[Co(edta)]^-$ after Jordan *et al.*[10)] The tn compound was prepared from $[Co(CO_3)(tn)_2]ClO_4$ and malonic acid. Found: N, 13.46; C, 26.46; H, 5.42%. Calcd for $[Co(mal)(tn)_2]ClO_4$: N, 13.71; C, 26.45; H, 5.43%. The bis(phen) compound was synthesized from $[CoCl_2(phen)_2]Cl\cdot 3H_2O$[11)] and sodium malonate in aqueous solution. The solution was heated on a water bath until the color of the solution changed to red and then filtered while hot. Cooling the filtrate to room temperature yielded needle-like crystals. These were recrystallized from warm water and suction filtered. Found: N, 8.37; C, 48.41; H, 3.67%. Calcd for $[Co(mal)(phen)_2]Cl\cdot NaCl\cdot 3H_2O$: N, 8.37; C, 48.45; H, 3.61%. The absorption maximum in water was at 510 nm ($\varepsilon=94$). The bipyridine compound, $[Co(mal)(bpy)_2]Br\cdot H_2O$,[5)] was prepared by a method similar to that for the phen compound. Since the chloride salt was too soluble to obtain good crystals and the iodide and perchlorate were too insoluble to allow NMR measurements, the complex was obtained in the bromide by adding excess potassium bromide to the hot, filtered reaction mixture and cooling in ice. This procedure gave the crystals of the composition consistent with $[Co(mal)(bpy)_2]Br\cdot 0.5KBr\cdot H_2O$. Recrystallization from warm water gave an analytically pure compound, for which the identity was confirmed by the visible absorption and NMR spectra, and by chemical analysis.[5)]

Measurements. The solubilities of the $(N)_4$ compounds were rather small; they are about 0.10, 0.22, 0.084, 0.16, and 0.05 mol dm^{-3} for the en, tn, phen, bpy, and tetraammine complexes, respectively. Therefore these complexes were dissolved in deuterium oxide to near saturation.

Nuclear magnetic resonance spectra were taken at 36.4 °C on a Varian T-60 spectrometer operating at 60 MHz. Owing to the low solubilities of the $(N)_4$ compounds, we measured the peak height (rather than integrated intensity) of the malonate singlet at suitable time intervals after dissolution. The exchange rates were obtained from the slope of the plots of ln(intensity) *vs.* time. Chemical shifts were referred to internal sodium 2,2-dimethyl-2-silapentane-5-sulfonate (DSS). The stability of these complexes against acid- and base-hydrolysis could be checked easily by NMR spectra thanks to the fact that the chemical shifts of coordinated malonates and the uncoordinated malonic acid or malonate anion are different.

The solution pD was adjusted by appropriate amount of HCl or Na_2CO_3 and measured by a Hitachi-Horiba Model F-7 pH meter with a microelectrode accessory, immediately after kinetic measurements. The pH meter readings were converted to the pD values by the empirical formula developed by Fife and Bruice,[12)] pD=pH(meter readings)+0.35(at 36.4 °C).

Absorption spectra were run on a Shimadzu UV-200 double beam spectrophotometer and circular dichroism spectra on a JASCO J-40CS spectropolarimeter.

Results and Discussion

The NMR spectrum of the pentaammine compound was reported previously for dimethyl-d_6 sulfoxide solution.[8c)] In D_2O the compound gave a sharp peak at δ 3.41 due to coordinated malonate and two broad absorptions at δ 3.79 and 2.84 with an intensity ratio of 4:1. The latter two absorptions are due to coordinated *cis* and *trans* (to coordinated oxygen) ammine groups and their chemical shift differences are explained by the magnetic anisotropy of the central cobalt(III) ion.[13)] Figure 1 shows the NMR spectra of the $(N)_4$ complexes used in this work, taken in pure deuterium oxide and the chemical shift values are summarized in Table 1. The malonate hydrogens of the $(N)_4$ compounds appear as a singlet between $\delta=3.19$ and 3.33. The tetraammine compound exhibits two broad absorptions at $\delta=4.23$ and 3.29 with equal intensities and they are due to coordinated ammine groups. The high field signal at $\delta=3.29$ can be assigned to ammine groups *trans* to the oxygen atoms of coordinated malonate ion on the basis of the magnetic anisotropy effect of the cobalt(III) ion.[13)] The spectrum of the en compound has been reported[2,3,7)] and consists of four peaks at $\delta=5.25$ (*cis* NH_2), 4.49 (*trans* NH_2), 3.32 (malonate CH_2), and 2.62 (CH_2CH_2 of en). The tn compound showed, in addition to malonate resonance, two broad peaks at $\delta=4.70$ (*cis* NH_2) and 4.07 (*trans* NH_2) and two complex multiplets at about $\delta=2.57$ (C_1 and C_3 methylenes) and 1.87 (C_2 methylene). The latter two methylene peaks sharpen as the deuteration at NH_2 groups proceeds, as shown in the inset of Fig. 1. The assignment of the NH_2 resonances of the en and tn compounds has been made previously[13)] and the high-field signals are due to *trans* NH_2 groups. In the pentaammine, tetraammine, bis(en), and bis(tn) compounds, all the ammine and amine groups undergo hydrogen-deuterium exchange in basic deuterium oxide.[14)] The resonances due to phen and bpy ligands appear in fine structures between $\delta=9.15$ and 7.12, and $\delta=8.96$ and 7.32, respectively.

Exchange Reaction of the $(N)_4$ Compounds. The malonate singlet of all the compounds examined here decreased in intensity with time. The ln(intensity) *vs.* time plots gave a straight line, indicating that the deuteration process follows the kinetic equation

$$-\frac{d}{dt}[\mathrm{Co\ mal_H}] = -k[\mathrm{Co\ mal_H}],$$

where $[\mathrm{Co\ mal_H}]$ is the concentration of an undeuterated malonatocobalt(III) complex and k is the pseudo-first-order rate constant for the deuteration of malonate ligand. In Fig. 2, the log(k) values are plotted against the solution pD. The solid lines in Fig. 2 have slopes of +1 and −1. Though the low solubilities of the $(N)_4$ compounds made the quality of the pD-rate

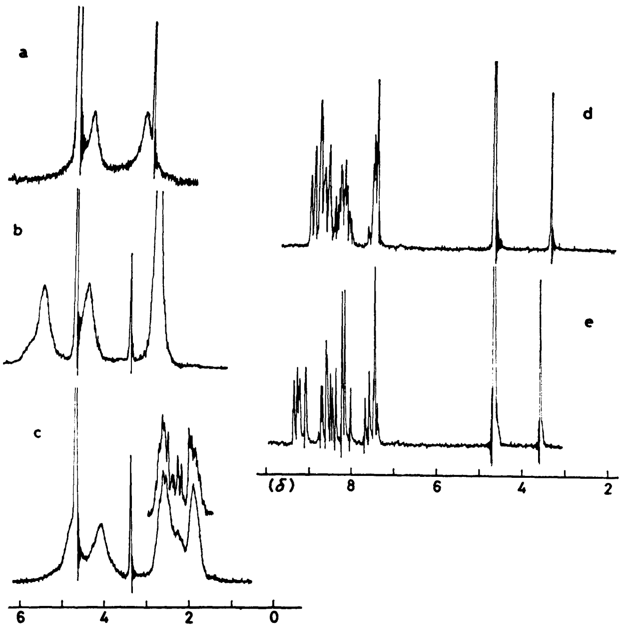


Fig. 1. The 60 MHz NMR spectra of $[Co(mal)(N)_4]^+$ complexes in deuterium oxide, where $(N)_4$ is (a) $(NH_3)_4$, (b) $(en)_2$, (c) $(tn)_2$, (d) $(bpy)_2$, and (e) $(phen)_2$. Inset of (c) illustrates the spectrum after complete deuteration of all NH_2 groups of tn. The strong peak at δ 4.62 is due to solvent HDO.

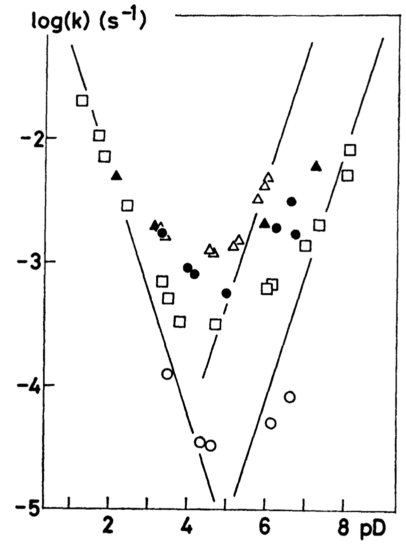


Fig. 2. The log(k) *vs.* pD plots for the deuteration of malonate hydrogens of $[Co(mal)(N)_4]^+$ complexes, where $(N)_4$ is $(NH_3)_4$ (○), $(tn)_2$ (□), $(en)_2$ (●), $(phen)_2$ (△), and $(bpy)_2$ (▲). Solid lines are with slopes of +1 or −1.

Table 1. Chemical shifts measured in deuterium oxide

The values are in δ (ppm) from an internal DSS.

	$(NH_3)_4$	$(en)_2$	$(tn)_2$	$(phen)_2$	$(bpy)_2$	$(NH_3)_5$
Malonate	3.19	3.32	3.33	3.28	3.32	3.41
cis Amine or ammine	4.23	5.25	4.70			3.79
trans Amine or ammine	3.29	4.49	4.07			2.84
Others		2.62[a)]	2.57[b)] 1.87[c)]	9.15∼7.12[d)]	8.96∼7.32[e)]	

a) CH_2CH_2. b) C_1 and C_3 methylenes. c) C_2 methylene. d) phen. e) bpy.

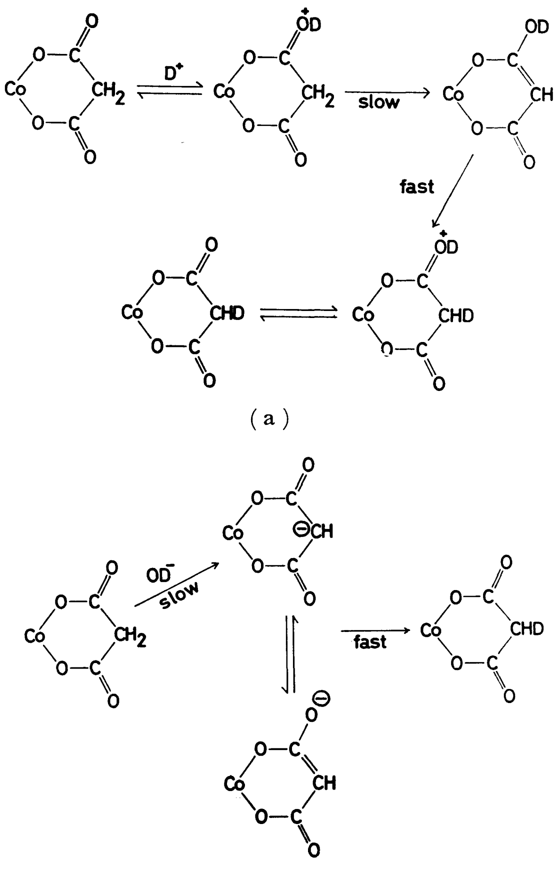
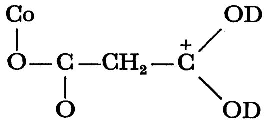


Fig. 3. A probable mechanism of hydrogen-deuetrium exchange catalysed by (a) D_3O^+ and (b) OD^- ions.

profile rather poor, Fig. 2 indicates that log(k) is proportional to $-$pD at lower pD while at higher pD it is proportional to pD. From this pD dependence it follows that k is proportional to $[D_3O^+]$ at lower pD and to $[OD^-]$ at higher pD. Therefore, the exchange reaction is acid-catalysed at pD values less than about 4 and base-catalysed at higher pD.

The mechanism of acid-catalysed deuteration will be considered in an analogous way to that proposed for the deuteration of glycine residues in $[Co(edta)]^-$ ion.[15,16] Farago and Smith[5] proposed such a mechanism as illustrated in Fig. 3(a). In this mechanism, the initial step is the rapid protonation of carbonyl oxygen, which is followed by the rate-determining step of a hydrogen abstraction to give an enol. This enol will tautomerize, upon deuteration, to regenerate the carboxyl group. The deuteration is thus effected by D_2O molecule donating D^+ to the enol intermediate.

The second mechanism proposed originally by Terrill and Reilley[15] also for $[Co(edta)]^-$ involves the carbonyl protonation and the subsequent rupture of carboxylate-cobalt bond. This mechanism seems at first sight to be adapted to the present case. Since this mechanism assumes the monodentate carbonium ligand of the form,



$$\mathrm{\underset{\underset{\displaystyle O}{|}}{\overset{\overset{\displaystyle Co}{|}}{O}}-\underset{\underset{\displaystyle O}{|}}{C}-CH_2-\overset{+}{C}\begin{matrix}\diagup OD\\ \diagdown OD\end{matrix}}$$

we may reasonably expect concomitant racemization at the metal center. For $[Co(edta)]^-$ ion, Terrill and Reilley in fact confirmed that deuteration is accompanied by racemization. For the optically active en compound, however, we did not observe any measurable change in the circular dichroism spectrum over the whole pD region examined here and over several half-lives of deuteration. In highly basic solution, this ion undergoes base-hydrolysis and decreases its optical activity as reproted by Farago and Keefe.[17] Though both mechanisms are consistent with the $[D_3O^+]$ dependence of the rate constant, the second mechanism does not seem to play the dominant role in our systems.

The mechanism of base-catalysed reaction will involve the carbanion intermediate, see Fig. 3(b). The first step may be a hydrogen abstraction by OD^- to give the carbanion. This carbanion can be resonance stabilized with the enol form, which favors the planar structure of the malonate moiety of this intermediate. The rate-determining step in base-catalysed reaction will be the C–H bond rupture. As for the acid-catalysed reaction, the deuteration is effected by D_2O donating D^+ to the carbanion intermediate. For the en and bpy compounds, Farago and Smith[5] made temperature dependence studies between 20 and 37 °C at around pD=2 to 3. Their results at 37 °C are in good agreement with our data shown in Fig. 2. Figure 2 indicates also that in acid-catalysed reaction the rates for all the compounds are not so different but in base-catalysed reaction the rates vary from compound to compound and the rate is in the order $(phen)_2$—$(bpy)_2 > (en)_2 > (tn)_2 > (NH_3)_4$.

Deuteration Reaction of The Pentaammine Compound. Figure 4 shows the log(k) *vs.* pD plots for $[Co(malH)(NH_3)_5]^{2+}$ ion. This plots contrast with Fig. 2 in the following points; (i) the deuteration is base-catalysed even at lower pD values, (ii) at about pD=3.95, the rate constant steps down to a value of 5×10^{-5} s^{-1}, and (iii) at higher pD region the rate constant does not depend on acid or base concentration. Clearly the sudden decrease at pD=3.95 corresponds to the deprotonation of the unidentate malonate ligand, for which the pK_a value was estimated by Svatos and Taube[8a] at 3.41(μ=0.1). By applying the deuterium

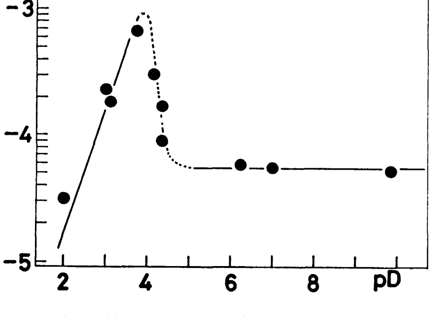


Fig. 4. The log(k) *vs.* pD plots for the deuteration of malonate in $[Co(OOCCH_2COOH)(NH_3)_5]^{2+}$. Solid lines are with slopes of +1 or zero.

isotope effect of 0.35 pH meter unit[12] to 3.41, we obtain the value 3.76. This value compares well with the pD value that corresponds to the kink in the pD-rate profile of Fig. 4. At low pD, the reaction should involve the coordinated carbanion intermediate produced by hydrogen abstraction by OD^- catalyst. The pD-independent rate at high pD region suggests that the methylene group in the $[Co(OOCCH_2COO)(NH_3)_5]^+$ ion undergoes either "water-catalysed" exchange or mixed D^+–OD^- (zwitterionic) catalysed exchange. The deuteration of methylene group of free ethyl malonate anion has been studied by Kirby and Lloyd[18] and the observed pH-independent exchange rate is reported at $3.33\times10^{-4}\,s^{-1}$ at 39.6 °C. This value is approximately an order of magnitude larger than our corresponding value for the Co(III)-$OOCCH_2COO^-$ group. In this context, the effect of the electron-withdrawing power of the cobalt(III) ion upon the exchange rate does not appear significant.

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4) Abbreviations; mal=malonate dianion, malH=malonate monoanion, en=ethylenediamine, tn=1,3-propanediamine, phen=1,10-phenanthroline, bpy=2,2′-bipyridine, edta=ethylenediaminetetraacetate.

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