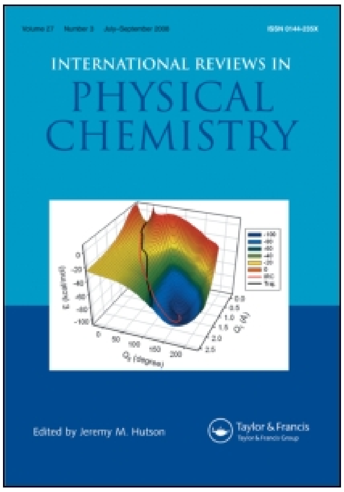

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Unusual kinetics of gas-phase proton transfer to $Mn(CO)_5^-$ and $Re(CO)_5^-$*

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Rate constants for gas-phase proton transfer to $Mn(CO)_5^-$, $Re(CO)_5^-$ and Cl^- from reference acids and metal hydrides are determined. Proton-transfer efficiencies to $Mn(CO)_5^-$ are small, and less than the efficiencies for proton transfer to Cl^-; proton-transfer efficiencies to $Re(CO)_5^-$ are larger than those for $Mn(CO)_5^-$, but still generally less than for transfer to Cl^-. Proton-transfer efficiencies to $Mn(CO)_5^-$ and $Re(CO)_5^-$ are substantially more dependent on the nature of the proton donor (e.g. metal hydride versus oxy-acid). The thermoneutral proton transfer between $Mn(CO)_5^-$ and ^{13}CO-labelled $HMn(CO)_5$ is particularly inefficient, occurring only in about 1 in 100 collisions. The results are discussed in view of evidence for a short lifetime of the collision complex, and the effects of electronic and structural reorganization of $Mn(CO)_5^-$ and $Re(CO)_5^-$, including loss of fluxionality of the metal species, which occur on protonation.

1. Introduction

We report here the kinetics of gas-phase proton transfer to the 18-electron anions $Mn(CO)_5^-$ and $Re(CO)_5^-$, which show that proton transfer to these ions is inefficient, even when highly exergonic (free energy decrease nearly 20 kcal mol^{-1}). This is in contrast to proton transfer reactions for a great many gas-phase ion/molecule reactions, which are typically 50% efficient if thermoneutral, and become 100% efficient if even slightly (4 kcal mol^{-1}) exergonic [1]. Our studies were prompted by the thermodynamic and kinetic measurements of proton-transfer involving metal hydrides in solution by Norton and co-workers [2], and also by Protasiewicz and Theopold [3]. These studies showed that rates of deprotonation of acidic transition metal hydrides, including $HMn(CO)_5$ and $HRe(CO)_5$, by nitrogen and oxygen bases in solution are slow. Rates of protonation of the conjugate anions are generally slower, and rates of

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* This paper is dedicated to Professor Michael Henchman, whose inimitable style and critical analysis have enlivened the field of ion/molecule chemistry.

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self-exchange between a hydride and its conjugate anion even more so. Some early work on $HMn(CO)_5$, $HCo(CO)_4$ and $H_2Fe(CO)_4$ showed indications that these trends were also evident in the gas phase, but were complicated by difficulties in handling the compounds, and the lack of reference acids with comparable acidities to the carbonyl hydrides [4]. This present gas-phase study has been made possible by recent determinations of quantitative acidities for strong acids [5–9], including our determination of the gas-phase acidities of $HMn(CO)_5$ and $HRe(CO)_5$ [10, 11].

The majority of the gas-phase acidities have been determined by equilibrium methods, and there is little available on the kinetics of gas-phase proton transfer involving anionic species, although a few exceptions exist [7, 8, 10–19]. We therefore needed to establish some basis for comparison of the kinetics of reactions of $Mn(CO)_5^-$ and $Re(CO)_5^-$ to be able to conclude whether they were 'normal', or showed exceptional behaviour. Proton-transfer efficiencies for reactions of $Mn(CO)_5^-$ and $Re(CO)_5^-$ can be compared to those of Cl^-, which was chosen as a reference anion since it is a closed-shell, monatomic anion for which the proton-transfer reactions are all highly exergonic. Variations in the rate constants for proton transfer to Cl^- might be expected to reflect the rate-determining factors intrinsic to the reference acid. This does *not* necessarily mean that the rate determined for Cl^- is collisional—for example, the reaction rate constant with HI corresponds to an efficiency of only 0·55 [12].

2. Experimental section

The proton-transfer reactions were studied using a flowing afterglow/Langmuir probe (FALP) [20], which has been described in earlier publications. The FALP apparatus has a high resolution mass spectrometer, necessary to resolve the isotopically labelled $HMn(CO)_5$, and to distinguish $Mn(CO)_5^-$ and $Re(CO)_5^-$ from species of quite similar masses (e.g. $Mn_2(CO)_3^-$ and $ReMn(CO)_3^-$, respectively). The helium buffer gas for these experiments was held at a pressure of 0·30–1·30 Torr (no variation with pressure was observed) and at 300 (± 3) K.

The complex $ReMn(CO)_{10}$ was introduced by passing argon or helium through the powdered solid sample held in a glass bubbler located after the flow meter, and used to make $Mn(CO)_5^-$ and $Re(CO)_5^-$ [21]. $Mn_2(CO)_{10}$ could also be used to make $Mn(CO)_5^-$. Cl^- was formed from CH_3Cl or CF_3Cl.

The reactant neutral concentration is determined from the flow rate measured with a heat-transfer type flow meter, calibrated for N_2. A conversion factor for other gases depends on the heat capacity of the flowing gas. The conversion factors for the metal hydrides were found to be $0{\cdot}20 \pm 0{\cdot}03$, as given elsewhere [10]. Flow meter calibration factors for the neutral acids were determined by known heat capacities for HBr and HI [22] or estimated heat capacities for CHF_2CO_2H, $CF_3C(O)CH_2C(O)CH_3$, CF_3CO_2H, $CF_3C(O)SH$ and $CF_3C(O)CHC(OH)CF_3$ [23].

Error limits for the rate constants are typically 35%. This is somewhat larger than typical for this instrumentation, as they reflect errors in the flow meter calibrations, possibilities of impurities in the neutral reactants, and difficulties in handling the low vapour pressure, often quite 'sticky' reagents. Relative rate constants between each of the different anions compared to the same neutral reactant are typically accurate to 10%.

$HMn(CO)_5$, $HRe(CO)_5$, $HMn(PF_3)_5$, $HCo(PF_3)_4$ and $ReMn(CO)_{10}$ were synthesized by slight modifications [10] of literature procedures [24–27]. ^{13}CO-labelled $HMn(CO)_5$ was synthesized by thermal and photochemical substitution of ^{13}CO for

CO, by transferring 3 g of $HMn(CO)_5$ into a 1-litre pyrex bulb (equipped with a cold finger and closed with an FETFE-o-ring-sealed Teflon stopcock) and adding ~ 1–2 atmospheres of ^{13}CO. The liquid metal complex was protected from light and stirred vigorously to promote mixing with the volatized complex. The reaction flask was placed in a sunny window for 4 weeks, and then the metal complex separated from the CO by cooling the sample in dry ice/acetone and removing the CO by vacuum transfer. The bulb was again filled by ~ 1–2 atmospheres of ^{13}CO, and reacted for 8 weeks, and again separated from the CO. Each of the metal hydrides was dried thoroughly over P_2O_5, and purified by vacuum transfer. The metal hydrides were cooled to dry ice/acetone temperature and degassed immediately prior to use. HI was purified by trap-to-trap distillation immediately prior to use. The HI initially acts only to displace residues on the inlet systems, thus we had to flow HI until no impurity ion products showed in the mass spectrum, and the observed rate of reaction was reasonably constant in successive data sets. All other reagents were purchased from commercial sources and used as supplied, except for degassing at liquid nitrogen temperature.

3. Results

Rate constants, k_{expt}, for reaction of $Mn(CO)_5^-$, $Re(CO)_5^-$ and Cl^- are given in table 1. A few of the rate constants have been reported by us elsewhere [10, 11 (*a*)]. Also given in table 1 are the rate constants for reaction of Cl^- with HBr and HI reported by Zwier *et al.* [12]. Our rate constant for reaction with HBr was consistently higher (although within the error limits of each determination). The rate constant we measured for reaction of Cl^- with the HI, even with attempts to purify the HI, was still about a factor of 5 below that reported by Zweir *et al.*; we normalized our rate constants for reaction of $Mn(CO)_5^-$ and $Re(CO)_5^-$ by this factor.

All reactions of $Mn(CO)_5^-$, $Re(CO)_5^-$ or Cl^- with the 11 acids of table 1 proceed solely by proton transfer to give the conjugate anion of the reference acid.

The gas-phase acidities, $\Delta G^\circ_{\mathrm{acid}}$, of the acids [5, 6, 9, 10, 22] are given in table 2. The gas-phase acidity of ^{13}CO-labelled $HMn(CO)_5$ is assumed to be equal that of unlabelled $HMn(CO)_5$, since the ^{13}CO labelling will have minimal effect on the CO vibrational frequencies, and further, the acidity is affected only by the change in those frequencies with deprotonation. The $\Delta H^\circ_{\mathrm{acid}}$ of each of the acids studied are also given in table 2 for reference purposes. It is emphasized that in all cases except those for HCl, HBr and HI, the $\Delta S^\circ_{\mathrm{acid}}$ are estimated, and the $\Delta H^\circ_{\mathrm{acid}}$ given in table 2 have substantially larger error limits than the $\Delta G^\circ_{\mathrm{acid}}$. This is particularly true for the pentanediones, $CF_3C(O)CH_2C(O)CH_3$ and $CF_3C(O)CH_2C(O)CF_3$, and the metal hydrides. In all cases here, exergonic reactions are exothermic, and endergonic reactions endothermic, that is, there is no evidence that the entropy change for the proton-transfer reaction plays a direct role in the kinetics (as has been observed for some reactions [18]). In part because of the disparity in the types of proton donors, and therefore large errors in relative $\Delta H^\circ_{\mathrm{acid}}$, only the gas-phase acidities, $\Delta G^\circ_{\mathrm{acid}}$, are considered in comparing the rate constants to the available thermodynamic driving forces.

Collisional rate constants for the reactions, k_{coll}, were calculated using the paramatrized trajectory method of Su and Chesnavich [28]; the polarizabilities and dipole moments used for the reactant acids are summarized in table 2 [29–35]. Reaction efficiencies, $k_{\mathrm{expt}}/k_{\mathrm{coll}}$, were calculated and are given in table 1 for each

Table 1. Rate constants for proton-transfer reactions of $Mn(CO)_5^-$, $Re(CO)_5^-$ and Cl^-.[a]

	$Mn(CO)_5^-$		$Re(CO)_5^-$		Cl^-	
Reactant acid	Rate constant	Efficiency[b]	Rate constant	Efficiency[b]	Rate constant	Efficiency[b]
HCl	—	—	0·015	0·015	—	—
CHF_2CO_2H	—	—	0·22	0·16	1·1	0·49
$CF_3C(O)CH_2C(O)CH_3$	—	—	0·018	0·011	3·2	1·0
HBr	0·0011	0·0013	0·56	0·74	0·96 0·75 (±0·10)[c]	0·79
CF_3CO_2H	0·027	0·018	0·37	0·27	0·98	0·41
$HMn(CO)_5$—^{13}C-labelled	0·0088	0·0085	0·15	0·16	1·6	0·87
$CF_3C(O)SH$	0·43	0·23	0·46	0·27	2·3	0·75
$CF_3C(O)CH_2C(O)CF_3$	0·26	0·16	0·82	0·56	1·3	0·42
HI	0·32	0·47	0·37	0·59	0·63 (±0·09)[c]	0·55
$HMn(PF_3)_5$	0·0033	0·0037	0·13	0·17	—	—
$HCo(PF_3)_4$	0·37	0·41	0·35	0·45	1·0	0·55

[a] All rate constants are in units of 10^{-9} cm^3 $molecule^{-1}$ s^{-1}, and were determined at 297–303 K and 0·30–1·30 Torr helium buffer pressure. Errors in the experimental rate constants are ~ 35%.

[b] Reaction efficiencies are given by k_{expt}/k_{coll}, with k_{coll} calculated by the method of Su and Chesnavich [28] using polarizabilities and dipole moments from table 2.

[c] Zweir *et al.* [12].

Table 2. Gas-phase acidities, (ΔG°_{acid} and ΔH°_{acid}), polarizabilities (α), and dipole moments (μ) for molecules used in this study.

Acid	ΔH°_{acid} (kcal/mol^{-1})	ΔG°_{acid} (kcal/mol^{-1})	Reference	α (10^{-24} cm^3)	Reference	μ (Debye)	Reference
HCl	333·3±0·2	327·9±0·5	[22]	2·63	[29]	0·82	[30]
$HRe(CO)_5$	332·6±3·8	323·9±2·4	[10]	—		—	
CHF_2CO_2H	330·8±2·3	323·8±2·0	[9, 6]	5·28	[31]	2·10	*a*
$CF_3C(O)CHC(OH)CH_3$	328·4±4·1	322·0±2·0	[9, 5]	11·4	[31]	3·0	*b*
HBr	323·5±0·2	318·3±0·4	[22]	3·61	[29]	0·82	[30]
CF_3CO_2H	323·3±2·3	316·3±2·0	[9]	5·66	[31]	2·28	[32]
$HMn(CO)_5$	322·5±3·7	313·8±2·3	[10]	16·1	*c*	0·70	[33]
$CF_3C(O)SH$	318·6±3·0	312·5±2·0	[9]	8·3	*d*	3·0	*d*
$CF_3C(O)CHC(OH)CF_3$	316·7±4·1	310·3±2·0	[9]	11·5	[31]	3·0	*b*
HI	314·4±0·1	309·3±0·4	[22]	5·4	[29]	0·44	[30]
$HMn(PF_3)_5$	309·4±4·9	300·1±3·5	[10]	20	*e*	0·3	*e*
$HCo(PF_3)_4$	301·4±7·2	295·7±5·8	[10]	18·7	*f*	0·3	*f*

[a] Dipole moment estimated from that of CH_3CO_2H (1·74 D, [32]) and CF_3CO_2H (2·28 D, [32]).

[b] Estimated to be the same as $CH_3C(O)CH_2C(O)CH_3$ [32].

[c] Polarizability calculated from the index of refraction and density [33].

[d] Polarizability estimated by comparison to CH_3CO_2H (5·16), CF_3CO_2H (5·66), and $CH_3C(O)SH$ (7·8) [31], and dipole moment estimated from similar molecules [32].

[e] Polarizability estimated to be slightly greater than that of $HCo(PF_3)_4$, and dipole moment estimated about that of $HCo(PF_3)_4$.

[f] Polarizability estimated to be equal to that of $Ni(PF_3)_4$, calculated from the index of refraction and density [34], and the dipole moment estimated to be less than that of $HMn(CO)_5$ (0·70 D, [33]), based on the crystal structure [35].

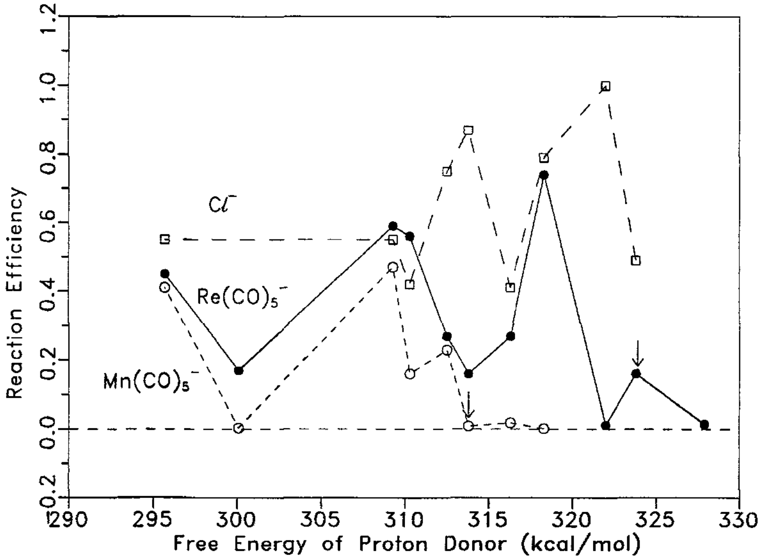

Figure 1. Efficiency of proton transfer to $Mn(CO)_5^-$, $Re(CO)_5^-$ and Cl^- as a function of the free energy of the proton donor, ΔG°_{acid}. The exergonicity increases to the left; the point of thermoneutral proton transfer is indicated with an arrow for $Mn(CO)_5^-$ and $Re(CO)_5^-$.

reaction. The reaction efficiencies for proton transfer to $Mn(CO)_5^-$, $Re(CO)_5^-$ and Cl^- are shown for each reaction in figure 1, as a function of ΔG°_{acid} of the reactant acid.

The most dramatic data point is the extremely low efficiency, only 0·0085, for the thermoneutral proton transfer between $Mn(CO)_5^-$ and $HMn(^{13}CO)_5$—proton transfer takes place on less than 1 in every 100 collisions. Extremely small efficiencies for reaction of $Mn(CO)_5^-$ and HBr and CF_3CO_2H are due to the positive free energy change for the proton transfer. Reaction rate constants were not determined for reaction with HCl, CHF_2CO_2H or $CF_3C(O)CH_2C(O)CH_3$, since they all have significantly positive $\Delta G^\circ_{proton\ transfer}$, and the rate constants are too small to be measurable on this apparatus ($k \lesssim 10^{-12}$ cm^3 molecule^{-1} s^{-1}). Efficiencies for reaction of $Mn(CO)_5^-$ with the remaining five acids, for which the proton transfer is exergonic, are all less than 100 %, and are all smaller than for reaction of Cl^-. The least exergonic proton transfer (reaction with $CF_3C(O)SH$) is among the most efficient, and the efficiencies (or efficiency ratios) show no regular trend as a function of increasing exergonicity.

Proton transfer to $Re(CO)_5^-$ has a small positive $\Delta G^\circ_{proton\ transfer}$ for reaction with HCl, and is nearly thermoneutral in reaction with CHF_2CO_2H; all other reactions are exergonic. Reaction efficiencies are again low; for reaction of $Re(CO)_5^-$ with HBr and $CF_3C(O)CH_2C(O)CF_3$ the efficiencies are, however, comparable to those for reaction of Cl^-. For all cases where both the proton transfer to $Re(CO)_5^-$ and $Mn(CO)_5^-$ are exergonic, the efficiency for reaction of $Re(CO)_5^-$ is larger than those for reaction of $Mn(CO)_5^-$.

Proton transfer to Cl^- is generally more efficient than to $Mn(CO)_5^-$ or to $Re(CO)_5^-$. The variation of the efficiencies with the type of proton donor is much less than for the metal anions—only a factor of ~ 2, compared to a factor of ~ 500 for $Mn(CO)_5^-$ and a factor of ~ 5 for $Re(CO)_5^-$.

4. Discussion

For inefficient reactions, reaction efficiency often increases with increasing exergonicity of the proton-transfer process [17]. This effect is observed, for example, in the reaction of CH_3O^- with the series of alcohols CH_3OH, CH_3CH_2OH, $(CH_3)_3COH$ and CF_3CH_2OH [17]. Previous gas-phase studies of proton-transfer rates involving transition metals have been reported only for the positive-ion systems $Fe(CO)_5/Fe(CO)_5H^+$ [36] and Cp_2Fe/Cp_2FeH^+ [37, 38], both of which undergo protonation/deprotonation at rates less than collisional. Efficiencies for proton transfer to ferrocene show a very strong dependence on the type of proton donor [37]. If the reaction efficiencies are compared only for a homologous series of donors then a regular increase in proton-transfer efficiency with increasing exergonicity of the proton transfer is observed. For proton transfer to Cp_2Fe one such homologous series is ring-protonated aromatics (e.g. protonated benzene, anisole, hexamethylbenzene) and another is oxygen-protonated donors (protonated acetone and acetophenone); the oxygen-protonated donors have faster rates for the same exergonicity as the ring-protonated donors. Proton-transfer kinetics were investigated only for the reaction of $Fe(CO)_5H^+$ with mesitylene [36].

In the reactions of $Mn(CO)_5^-$ and $Re(CO)_5^-$, the entire set of proton donors clearly do not constitute a set of homologous donors. Based on their similar chemical structures, one might expect that $CF_3C(O)CH_2C(O)CF_3$ and $CF_3C(O)CH_2C(O)CH_3$ are homologous donors, and indeed, the reaction efficiency for the $Re(CO)_5^-$ reaction with $CF_3C(O)CH_2C(O)CF_3$ (the more exergonic reaction) is greater than that for $CF_3C(O)CH_2C(O)CH_3$. However, reaction of $Re(CO)_5^-$ with HBr has a greater efficiency than with HI. There are too few proton donors with greater acidities than $HMn(CO)_5$ to make similar comparisons. Surprising to us was the fact that the three hydrides $HMn(CO)_5$, $HMn(PF_3)_5$ and $HCo(PF_3)_4$ do not constitute a homologous series (as defined by the increase in efficiency with increasing exergonicity of the proton transfer). Reaction of $Mn(CO)_5^-$ shows comparable, extremely small efficiencies for reaction with $HMn(CO)_5$ and with $HMn(PF_3)_5$—despite $\Delta G^{\circ}_{\text{proton transfer}}$ of nearly -14 kcal mol^{-1} for the latter. Reaction of $Mn(CO)_5^-$ with $HCo(PF_3)_4$ is over an order of magnitude more efficient (for $\Delta G^{\circ}_{\text{proton transfer}}$ of -18 kcal mol^{-1}) such that we do not consider this evidence of an increase in efficiency due solely to the increasing exergonicity. Similar effects are seen for reaction with $Re(CO)_5^-$; efficiencies for reaction with $HMn(CO)_5$ and $HMn(PF_3)_5$ are comparable, and the efficiency for reaction with $HCo(PF_3)_4$ is larger.

Reaction of Cl^- shows exactly the opposite behaviour with increasing exergonicity: the efficiency for reaction with $CF_3C(O)CH_2C(O)CF_3$ is smaller than that for reaction with $CF_3C(O)CH_2C(O)CH_3$, that for CF_3CO_2H is smaller than that for CHF_2CO_2H, and that for HI is smaller than that for HBr. The efficiencies for reaction with the metal hydrides are in the order $HMn(CO)_5 > HCo(PF_3)_4$—again the opposite of the behaviour shown by $Mn(CO)_5^-$ and $Re(CO)_5^-$.

Cl^- has been suggested to react with the hydrogen halides by a 'direct' mechanism, with a single-well potential in the collision complex. This view is supported by studies on the vibrational distribution of the resulting HCl product [12]. It appears from the data here that the decreasing reaction efficiencies with increasing exergonicity of the proton transfer are also an indication of the direct proton-transfer mechanism.

Dodd *et al.* [17] interpret an increasing efficiency with increasing exergonicity to be an indication of a double-well potential in the collision complex, in which the barrier to the proton transfer lies below the energy of the separated products or reactants. For the metal systems of interest here, the complete lack of information on the potential surfaces for proton transfer to $Mn(CO)_5^-$ or $Re(CO)_5^-$ precludes comparison to detailed dynamical models [39–41].

We can, however, provide a qualitative understanding of the efficiencies based on a double-well potential. The proton-transfer efficiency for the double-well potential can be related to the lifetime of the collision complex and to the time for the proton to 'jump' (transfer *within* the collision complex), such that the proton can transfer prior to dissociation of the complex [41, 42]. Evidence that the lifetime of the collision complex is quite short comes from the fact that we have not observed any association reactions of $Mn(CO)_5^-$ or $Re(CO)_5^-$ (or of $HMn(CO)_5$, $HRe(CO)_5$, or any of the other metal hydrides we have studied) under our experimental conditions [10, 43]. This is in contrast to the behaviour of other strong polyatomic acids (or their conjugate bases), for which association reactions at rates approaching collisional are ubiquitous when proton transfer is thermoneutral or endothermic [7, 8, 10]. The apparent short lifetime is undoubtedly related to the inability of the metal anion to hydrogen bond. Other indirect evidence for this comes from the finding that metal anions in solution do not contact ion-pair, and there is, at best, slight evidence that cationic proton donors may undergo limited hydrogen bonding to them [2]. Metal hydrides themselves do not have the ability to hydrogen bond, and all evidence indicates the hydrogen is negatively polarized [44]. We suspect this double jeopardy combination of metal anion and metal hydride lack of hydrogen bonding ability is the primary cause of the particularly low proton-transfer rates between them, especially evident in the $Mn(CO)_5^-/HMn(CO)_5$ self-exchange reaction. This has also been suggested as the reason behind the very slow kinetics of the self-exchange reactions in solution [2, 3].

Two effects are likely to act to decrease the rate of proton transfer within the collision complex. First, the geometry change from a trigonal bipyramidal (D_{3h}) $Mn(CO)_5^-$ [45] to pseudo-octahedral (C_{4v}) $HMn(CO)_5$ [46], accompanied by a change in electronic configuration from d^8 to $d^6\sigma^2$ with loss of charge delocalization, has been suggested by us [10, 11] and others [2] to slow the proton-transfer rates. Second, $Mn(CO)_5^-$ is a highly fluxional molecule; it undergoes Berry pseudorotation, in which the axial and equatorial ligands readily exchange sites at room temperature. Calculations [47] indicate an effective activation enthalpy for the fluxional process to be $\sim 1\ \text{kcal mol}^{-1}$ (similar to $Fe(CO)_5$ [48]). Since $HMn(CO)_5$ is *not* fluxional [49], the fluxionality must be lost in the collision complex, resulting in a decrease in the entropy, therefore an increase in the free energy of the transition state which would slow the proton transfer. Similar considerations for the electronic effects would hold for $Re(CO)_5^-$ and $HRe(CO)_5$, although there is no reason to expect them to be quantitatively the same. There are no data on the fluxionality of $Re(CO)_5^-$; limited data on other systems suggest a higher activation enthalpy for the exchange process [50], but this would probably still make $Re(CO)_5^-$ fluxional at room temperature.

Effects peculiar to each of the reference acids must be causing the variations in the efficiencies seen in figure 1. These effects probably include differences in steric congestion, or slight differences in hydrogen-bonding ability of the proton donors. For example, sulphur-containing reactants have been observed to give rapid rates and/or differing reactivity patterns in their reactions with transition metal species, both in the gas phase [36, 51] and in solution [52]. SH^- has also been found to be a *slower* reactant than other bases in proton abstraction reactions, attributed to the poorer ability of sulphur to form hydrogen bonds (as compared to oxygen and nitrogen bases) [14]. $CF_3C(O)CH_2C(O)CH_3$ and $CF_3C(O)CH_2C(O)CF_3$ adopt enol forms in the gas phase, in which the enol hydrogen hydrogen bonds to the keto oxygen, forming a six-member ring [53]. This structure may prevent the $Mn(CO)_5^-$ and $Re(CO)_5^-$ from abstracting the proton as efficiently (although this is not the case for Cl^-). Such issues are at this point pure speculation. Since $HRe(CO)_5$ is the least acidic of all the metal hydrides studied to date, we have a limited number of reference acids with which to react the metal anions, and consequently limited ability to correlate the trends with known properties of the acids.

5. Conclusions

The efficiencies of gas-phase proton transfer to $Mn(CO)_5^-$ and $Re(CO)_5^-$ are generally small, and smaller than the efficiencies for proton transfer to Cl^-. Proton-transfer efficiencies to $Mn(CO)_5^-$ and $Re(CO)_5^-$ are substantially more dependent on the nature of the proton donor (e.g. metal hydride versus oxy-acid). The thermoneutral transfer between $Mn(CO)_5^-$ and ^{13}CO-labelled $HMn(CO)_5$ is particularly inefficient, occurring only in about 1 in 100 collisions. These observations parallel those observed for these and other metal anions in solution, and indicate the slow kinetics of proton transfer are intrinsic to the anion/proton donor interaction.

The proton-transfer kinetics are most consistent with qualitative expectations for a double-well potential for the ion/molecule collision complex, in which the collision complex has short lifetime. The exact nature of the barrier to proton transfer within the collision complex cannot be determined. We suggest that the barrier is due to an energy barrier, the result of electronic and structural reorganization of the trigonal-bipyramidal anions on forming the octahedral hydride, and an entropy barrier, the result of the loss of fluxionality of the anions which occurs on protonation. The combination of these effects, particularly the inability to form a long-lived hydrogen bonded collision complex, is suggested to cause the extremely low efficiency for the thermoneutral proton transfer between $Mn(CO)_5^-$ and ^{13}C-labelled $HMn(CO)_5$.

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References

[1] (*a*) Bohme, D., Mackay, G. I., and Schiff, H. I., 1980, *J. chem. Phys.*, **73**, 4976; (*b*) Bohme, D., 1984, *Ionic Processes in the Gas Phase*, edited by M. A. Almoster Ferreira (Dordrecht: Reidel).

[2] (*a*) Jordan, R. F., and Norton, J. R., 1982, *J. Am. chem. Soc.*, **104**, 1255; (*b*) Jordan, R. F., and Norton, J. R., 1982, *ACS Symp. Ser.*, **198**, 403; (*c*) Moore, E. J., Sullivan, J. M., and Norton, J. R., 1986, *J. Am. chem. Soc.*, **108**, 2257; (*d*) Edidin, R. T., Sullivan, J. M., and Norton, J. R., 1987, *J. Am. chem. Soc.*, **109**, 3945; (*e*) Kristjánsdóttir, S. S., Moody, A. E., Weberg, R. T., and Norton, J. R., 1988, *Organometallics*, **7**, 1983; (*f*) Weberg, R. T., and Norton, J. R., 1990, *J. Am. chem. Soc.*, **112**, 1105; (*g*) Kristjánsdóttir, S. S., and Norton, J. R., 1990, *Acidity of Hydrido Transition Metal Complexes in Solution*, in *Transition Metal Hydrides: Recent Advances in Theory*

and Experiment, edited by A. Dedieu (New York: VCH); (*h*) Kristjánsdóttir, S. S., and Norton, J. R., 1991, *J. Am. chem. Soc.*, **113**, 4366; (*i*) Kristjánsdóttir, S. S., Loendorf, A. J., and Norton, J. R., 1991, *Inorg. Chem.*, **30**, 4470.

[3] (*a*) Protasiewicz, J. D., 1990, PhD thesis, Cornell University; (*b*) Protasiewicz, J. D., and Theopold, K. H., 1993, *J. Am. chem. Soc.*, **115**, 5559.

[4] Miller, A. E. S., and Beauchamp, J. L., 1991, *J. Am. chem. Soc.*, **113**, 8765.

[5] Cumming, J. B., and Kebarle, P., 1978, *Can. J. Chem.*, **56**, 1.

[6] Caldwell, G., Renneboog, R., and Kebarle, P., 1989, *Can. J. Chem.*, **67**, 611.

[7] Viggiano, A. A., Morris, R. A., Dale, F., Paulson, J. F., Henchman, M. J., Miller, T. M., and Stevens Miller, A. E., 1991, *J. phys. Chem.*, **95**, 1275.

[8] Viggiano, A. A., Henchman, M. J., Dale, F., Deakyne, C. A., and Paulson, J. F., 1992, *J. Am. chem. Soc.*, **114**, 4299.

[9] Koppel, I. A., Taft, R. W., Anvia, F., Zhu, S.-Z., Hu, L.-Q., Sung, K.-S., Desmarteau, D. D., Yagupolskii, L. M., Yagupolskii, Y. L., Ignat'ev, N. V., Kondratenko, N., Volkonskii, A. Y., Vlasov, V. M., Notario, R., and Maria, P.-C., 1994, *J. Am. chem. Soc.*, **116**, 3047.

[10] Miller, A. E. S., Miller, T. M., Rekha, G. K., Lambrecht, A. R., and Paulson, J. P., *J. Am. chem. Soc.*, (to be submitted).

[11] Slightly different $\Delta G^{\circ}_{\mathrm{acid}}$ and $\Delta H^{\circ}_{\mathrm{acid}}$ are given in earlier work, see reference [4] and: (*a*) Miller, A. E. S., Kawamura, A. R., and Miller, T. M., 1990, *J. Am. chem. Soc.*, **112**, 457; (*b*) Miller, A. E. S., and Miller, T. M., 1992, *Energetics of Organometallic Compounds*, edited by J. A. Martinho Simoes (Dordrecht: Kluwer).

[12] Zwier, T. S., Bierbaum, V. M., Ellison, G. B., and Leone, S. R., 1980, *J. chem. Phys.*, **72**, 5426.

[13] Weisshaar, J. C., Zwier, T. S., and Leone, S. R., 1981, *J. chem. Phys.*, **75**, 4873.

[14] Grabowski, J. J., De Puy, C. H., Van Doren, J. M., and Bierbaum, V. M., 1985, *J. Am. chem. Soc.*, **107**, 7384.

[15] Han, C.-C., and Brauman, J. I., 1989, *J. Am. chem. Soc.*, **111**, 6491.

[16] Barlow, S. E., Dang, T. T., and Bierbaum, V. M., 1990, *J. Am. chem. Soc.*, **112**, 6832.

[17] Dodd, J. A., Baer, S., Moylan, C. R., and Brauman, J. I., 1991, *J. Am. chem. Soc.*, **113**, 5942.

[18] Meot-Ner (Mautner), M., 1991, *J. phys. Chem.*, **95**, 6580.

[19] Berkowitz, J., Ellison, G. B., and Gutman, D., 1994, *J. phys. Chem.*, **98**, 2744, and references therein.

[20] Miller, T. M., Miller, A. E. S., Paulson, J. F., and Liu, X., 1994, *J. chem. Phys.*, **100**, 8841.

[21] Meckstroth, W. K., and Ridge, D. P., 1985, *J. Am. chem. Soc.*, **107**, 2281.

[22] Chase, M. W. Jr., Davies, C. A., Downey, J. R. Jr., Frurip, D. J., McDonald, R. A., and Syverud, A. N., 1985, *JANAF Thermochemical Tables*, *J. Phys. Chem. Ref. Data*, **14**, (suppl. 1).

[23] Stein, S. E., Rukkers, J. M., and Brown, R. L., 1991, *NIST Standard Reference Database 25. The NIST Structures & Properties Database and Estimation Program* (Gaithersburg, MD: National Institute of Standards and Technology).

[24] Warner, K. E., and Norton, J. R., 1985, *Organometallics*, **4**, 2150.

[25] Miles, W. J., and Clark, R. J., 1968, *Inorg. Chem.*, **7**, 1801.

[26] (*a*) Udovich, C. A., and Clark, R. J., 1969, *Inorg. Chem.*, **8**, 938; (*b*) Sternberg, H. W., Wender, I., Friedel, R. A., and Orchin, J., 1953, *J. Am. chem. Soc.*, **75**, 2717.

[27] Flitcroft, N., Huggins, D. K., and Kaesz, H. D., 1964, *Inorg. Chem.*, **3**, 1123.

[28] (*a*) Su, T., and Chesnavich, W. J., 1982, *J. chem. Phys.*, **76**, 5183; (*b*) Su, T., 1990, *J. chem. Phys.*, **89**, 5355.

[29] Miller, T. M., 1990, *Atomic and Molecular Polarizabilities*, in *Handbook of Chemistry and Physics, 71st Edn*, edited by D. R. Lide, Jr., (Boca Raton: CRC Press), p. **10**-193.

[30] Nelson, R. D. Jr.; Lide, D. R. Jr., and Maryott, A. A., 1990, *Selected Values of Electric Dipole Moments for Molecules in the Gas Phase*, in *Handbook of Chemistry and Physics, 71st Edn*, edited by D. R. Lide, Jr., (Boca Raton: CRC Press) p. **9**-6.

[31] From the molar refractivity, determined from the refractive index and density: Aldrich Catalog/Handbook of Fine Chemicals 1994–1995, Aldrich Chemical Co., Milwaukee, WI.

[32] McClellan, A. L., 1963, *Tables of Experimental Dipole Moments* (San Francisco: W. H. Freeman).

[33] Hieber, W., and Wagner, G., 1958, *Z. Naturforshch.*, **13b**, 339.

[34] Wilkinson, G., 1951, *J. Am. chem. Soc.*, **73**, 5501.

[35] Frenz, B. A., and Ibers, J. A., 1970, *Inorg. Chem.*, **9**, 2403.

[36] Allison, C. E., Cramer, J. A., Hop, C. E. C. A., Szulejko, J. E., and McMahon, T. B., 1991, *J. Am. chem. Soc.*, **113**, 4469.

[37] Ikonomou, M. G., Sunner, J., and Kebarle, P., 1988, *J. phys. Chem.*, **92**, 6308.

[38] Meot-Ner (Mautner), M., 1989, *J. Am. chem. Soc.*, **111**, 2830.

[39] Lim, K. F., and Brauman, J. I., 1991, *J. chem. Phys.*, **94**, 7164, and references therein.

[40] Lim, K. F., and Kier, R. I., 1992, *J. chem. Phys.*, **97**, 1072, and references therein.

[41] Meot-Ner (Mautner), M., 1991, *J. Am. chem. Soc.*, **113**, 862, and references therein.

[42] Henchman, M., Smith, D., and Adams, N. G., 1991, *Int. J. Mass Spectrom. Ion Processes*, **109**, 105.

[43] These include reaction of $Mn(CO)_5^-$ with $HMn(CO)_5$, CF_3CO_2H, HBr, or $CF_3C(O)SH$, and reaction of $HMn(CO)_5$ with $CF_3C(O)S^-$, $CF_3C(O)CHC(O)CF_3^-$, I^-, or PO_3^-, with an apparent bimolecular rate limit $k \lesssim 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1}.

[44] Kristjánsdóttir, S. S., Norton, J. R., Moroz, A., Sweany, R. L., and Whittenburg, S. L., 1991, *Organometallics*, **10**, 2357.

[45] Frenz, B. A., and Ibers, J. A., 1972, *Inorg. Chem.*, **11**, 1109.

[46] Kukolich, S. G., and Sickafoose, S. M., 1993, *Chem. Phys. Lett.*, **215**, 168, and references therein.

[47] Demuynck, J., Strich, A., and Veillard, A., 1977, *Nouv. J. Chim.*, **1**, 217.

[48] (*a*) DiCarlo, E. N., 1980, *J. Am. chem. Soc.*, **102**, 2205; (*b*) DiCarlo, E. N., Zurbach, E. P., and Clark, R. J., 1991, *J. Am. chem. Soc.*, **113**, 4474, and references therein.

[49] Nmr studies of $HMn(CO)_5$ include: Ireland, P. S., Deckert, C. A., and Brown, T. L., 1976, *J. Magn. Res.*, **23**, 485; Vancea, L., and Graham, W. A. G., 1977, *J. Organomet. Chem.*, **134**, 219; Nakano, T., 1977, *Bull. Chem. Soc. Jap.*, **50**, 661; Onaka, S., Sugawara, T., Kawada, Y., and Iwamura, H., 1982, *J. Chem. Soc., Dalton Trans.*, 257. See also Clark, R. J., and Busch, M. A., 1973, *Accts. chem. Res.* **6**, 246.

[50] Meakin, P., Muetterties, E. L., and Jesson, J. P., 1972, *J. Am. chem. Soc.*, **94**, 5271.

[51] Stevens Miller, A. E., Miller, T. M., Morris, R. A., Viggiano, A. A., Van Doren, J. M., and Paulson, J. F., 1993, *Int. J. Mass Spectrom. Ion Processes*, **123**, 205.

[52] Darensbourg, M. Y., Liaw, W.-F., and Riordan, C. G., 1989, *J. Am. chem. Soc.*, **111**, 8051.

[53] Andreassen, A. L., and Bauer, S. H., 1972, *J. Mol. Structure*, **12**, 381.