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Ion Chemistry and Gas-Phase Basicity of Nickelocene by Ion Cyclotron Resonance Spectroscopy

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The gas-phase ion chemistry of bis(η^5-cyclopentadienyl)nickel (nickelocene) is studied using the techniques of ion cyclotron resonance spectroscopy. Total rate constants for the reactions of the primary fragment ions at 70 eV are determined using trapped-ion methods. The long-lived nickelocene anion, $Ni(C_5H_5)_2^-$, is formed directly by electron attachment and is unreactive with a variety of simple molecules. Nickelocene is observed to be an exceptionally strong base in the gas phase. Equilibrium proton-transfer reactions are observed in mixtures of nickelocene with $(CH_3)_3N$ and $(C_2H_5)_2NH$, from which the gas-phase basicity or proton affinity (PA) is determined to be 218.9 ± 1.0 kcal/mol relative to $PA(NH_3) = 201 \pm 1$ kcal/mol. Attempts to determine the site of protonation were inconclusive. The ion chemistry and base strength of nickelocene and ferrocene are compared.

Introduction

While the ion–molecule reactions of organic and simple inorganic molecules have been extensively studied and characterized,[2] the ion–molecule reactions of organometallic complexes have, in comparison, received relatively little attention. Schumacher and Taubenest first observed the ions $Fe_2(C_5H_5)_3^+$ and $Ni_2(C_5H_5)_3^+$ in the mass spectrum of ferrocene and nickelocene, respectively, at a source pressure of 10^{-5} Torr.[3] It was later suggested that these ions may result from the fragmentation of a small amount of neutral metallocene dimer, rather than as the product of an ion–molecule reaction.[4] More recent investigations of the gas-phase ion chemistry of ferrocene, using both high-pressure mass spectrometry[5] and ion cyclotron resonance spectroscopy,[6] prove this supposition to be incorrect, however. Müller has studied ligand displacement processes such as illustrated in eq 1 for

$$L_nM^+ + L' \rightarrow L_{n-m}L'M^+ + mL \qquad (1)$$

various organometallic species L_nM^+.[7] The ion–molecule reactions of ions derived from $Fe(CO)_5$ with a variety of σ- and π-electron-donating ligands have been recently investigated.[8,9]

The present work describes an ion cyclotron resonance (ICR) study of the ion chemistry of nickelocene, both alone and in mixtures with other molecules. Because of its thermal stability and moderate vapor pressure,[10] nickelocene was chosen to compare with the results of our earlier study of the ion chemistry of ferrocene.[6] An attempt to study the ion chemistry of bis(η^5-cyclopentadienyl)chromium was unsuccessful, primarily because of the low vapor pressure of this substance at ambient temperatures. Of particular interest in our previous investigation of metallocene ion chemistry was the unexpectedly high base strength observed for ferrocene in the gas phase.[6] For comparison, the gas-phase basicity of nickelocene is determined in the present study. Previous investigations of the mass spectrometry[3,4,11–13] and photoelectron spectrum[14] of nickelocene provide information useful in interpreting our results.

Experimental Section

The theory and instrumentation of ICR mass spectrometry have been previously described.[2,15,16] This work employed an instrument built at Caltech equipped with a 15-in. electromagnet capable of a maximum field strength of 23.5 kG.

Nickelocene was prepared as described in the literature[17] and determined to be pure by melting point, ir, and conventional mass spectrometric techniques.[18] The sample was pulverized in a nitrogen drybox, sublimed before use, and degassed by several freeze–pump–thaw cycles; no impurities were evident in the ICR mass spectrum. The vapor pressure of nickelocene at room temperature (20–25 °C) is ~10^{-2} Torr,[10] which was adequate for all of the present experiments. The vapor from a sublimed crystalline sample was introduced into the spectrometer by means of the normal inlet system through a variable-leak valve. All other chemicals used in this study were obtained from commercial sources and used as supplied except for degassing with several freeze–pump–thaw cycles.

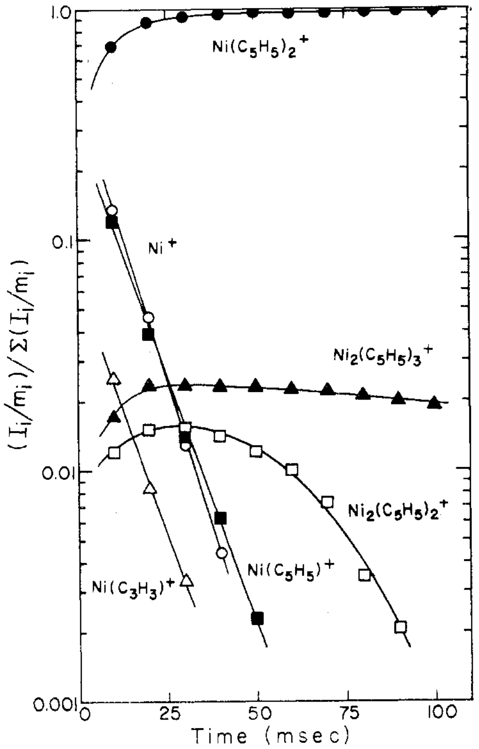


Figure 1. Temporal variation of ion abundance in nickelocene at 2.4 × 10^{-6} Torr following ionization by a 70-eV 10.0-ms electron beam pulse. The ^{58}Ni and ^{60}Ni isotopic ion abundances are summed.

The low vapor pressure of nickelocene precluded the use of a MKS Baratron Model 90H1-E capacitance manometer to provide accurate pressure measurements as in previous studies.[6,19] The nickelocene pressure was estimated by assuming that the Schulz-Phelps type ion gauge used to measure low pressures has the same sensitivity for nickelocene and ferrocene. No difficulties were encountered in calibrating the gauge with ferrocene.[6] This introduces an estimated maximum error of ±50% into the reported rate constants for the ion-molecule reactions of nickelocene. All experiments were performed at ambient temperature (20-25 °C).

Results and Discussion

Mass Spectrometry of Nickelocene. Positive Ions. The 70-eV positive-ion ICR mass spectrum of nickelocene at 1.3 × 10^{-7} Torr is in good agreement with previous reported mass spectra.[11,12] The ions observed and their relative abundances are $Ni(C_5H_5)_2^+$ (37%), $Ni(C_5H_5)(C_4H_2)^+$ (2%), $Ni(C_5H_5)(C_3H_3)^+$ (<1%), $Ni(C_5H_5)^+$ (33%), $Ni(C_3H_3)^+$ (7%), and Ni^+ (20%). The parent ion predominates at all electron energies.

Negative Ions. The negative-ion ICR mass spectrum of nickelocene at 5.4 × 10^{-7} Torr agrees qualitatively with that reported by Begun and Compton.[12] The ions observed at 70 eV and their relative abundances are $Ni(C_5H_5)_2^-$ (92%) and $C_5H_5^-$ (8%). The majority of the $Ni(C_5H_5)_2^-$ species is formed by capture of low-energy electrons scattered and trapped in the ICR cell. Begun and Compton reported a lifetime of $Ni(C_5H_5)_2^-$ formed by thermal electron attachment of >100 μs.[12] By calculating the drift time of the ion through the ICR cell,[20] the lifetime of the $Ni(C_5H_5)_2^-$ ion is estimated to be >10 ms. The nickelocene anion appears to attach zero-energy electrons and to have an essentially infinite lifetime; the observed behavior is quite analogous to that of SF_6.[21]

Positive-Ion Chemistry of Nickelocene. Figure 1 presents the temporal variation of relative ion abundance for nickelocene at 2.4 × 10^{-6} Torr following a 70-eV, 10-ms electron beam pulse. Double-resonance experiments[2b,16] unambiguously identify the charge-exchange reactions 2-4 and the condensation reactions 5 and 6, as occurring in this system.

Table I. Ion-Molecule Reactions, Rate Constants, and Reaction Enthalpies in Nickelocene

Reaction	k^a	ΔH^b
$Ni^+ + Ni(C_5H_5)_2 \longrightarrow Ni(C_5H_5)_2^+ + Ni$	1.5 ± 0.8	−33 ± 3
$Ni(C_3H_3)^+ + Ni(C_5H_5)_2 \rightarrow Ni(C_5H_5)_2^+ + Ni(C_3H_3)$	1.4 ± 0.7	
$Ni(C_5H_5)^+ + Ni(C_5H_5)_2 \rightarrow Ni(C_5H_5)_2^+ + Ni(C_5H_5)$		−37 ± 8
$\rightarrow Ni_2(C_5H_5)_2^+ + C_5H_5$	1.3 ± 0.7	
$\rightarrow Ni_2(C_5H_5)_3^+$		

[a] Rate constants in units of 10^{-9} cm^3 $molecule^{-1}$ s^{-1}. [b] Values in kcal/mol.

$$Ni^+ + Ni(C_5H_5)_2 \longrightarrow Ni(C_5H_5)_2^+ + Ni \tag{2}$$

$$Ni(C_3H_3)^+ + Ni(C_5H_5)_2 \longrightarrow Ni(C_5H_5)_2^+ + Ni(C_3H_3) \tag{3}$$

$$Ni(C_5H_5)^+ + Ni(C_5H_5)_2 \begin{cases} \rightarrow Ni(C_5H_5)_2^+ + Ni(C_5H_5) & (4) \\ \rightarrow Ni_2(C_5H_5)_2^+ + C_5H_5 & (5) \\ \rightarrow Ni_2(C_5H_5)_3^+ & (6) \end{cases}$$

The parent ion $Ni(C_5H_5)_2^+$ is unreactive, a conclusion verified by lowering the electron energy to 10 eV, which is below the appearance potentials of Ni^+, $Ni(C_3H_3)^+$, and $Ni(C_5H_5)^+$,[11a,12] and noting that no reaction products occur out to *m/e* 460. As expected from the reaction scheme, processes 2-6, abundances of the Ni^+, $Ni(C_3H_3)^+$, and $Ni(C_5H_5)^+$ ions decrease exponentially with time. From the slopes of the lines in Figure 1 and the known pressure of $Ni(C_5H_5)_2$, the total rate constants for the reactions of these three ions are calculated and summarized in Table I, along with reaction exothermicities where these can be estimated.[22] Although the process was not investigated, the minor product $Ni_2(C_5H_5)_2^+$ reacts further with $Ni(C_5H_5)_2$.

The charge-exchange reactions 2 and 4 may occur either with the formation of a symmetric intermediate, in which the two nickel atoms become equivalent, or under conditions such that the two nickel atoms remain distinct. These possibilities can be distinguished by determining the ratios for the double-resonance contribution from the reactant ions (e.g., $^{58}Ni(C_5H_5)^+$ and $^{60}Ni(C_5H_5)^+$) to the product ions $^{58}Ni(C_5H_5)_2^+$ and $^{60}Ni(C_5H_5)_2^+$.[23,24] Double-resonance experiments indicate that the charge-exchange reactions 2 and 4 do not proceed via a symmetric intermediate and that the Ni atom present in the product ion originates exclusively from the neutral reactant. A similar result is obtained for the reactions analogous to processes 2 and 4 in ferrocene.

Schumacher and Taubenest proposed a triple-decker sandwich structure for the $Ni_2(C_5H_5)_3^+$ ion,[3] which has more recently been observed by Hunt et al.[13] in the methane chemical ionization mass spectrum of nickelocene, together with the $Ni_2(C_5H_5)_2^+$ ion of reaction 5. The $Ni(C_5H_5)^+$ ion has been shown to react with $Ni(C_5H_5)_2$ in solution to produce the $Ni_2(C_5H_5)_3^+$ ion.[25] The triple-decker sandwich structure has been confirmed by x-ray structure analysis of tris(η^5-cyclopentadienyl)dinickel tetrafluoroborate.[26] In spite of the evidence for this structure, we find that the triple-decker sandwich is *not* an intermediate in reaction 4 since the two Ni atoms would be equivalent.

Negative-Ion Chemistry of Nickelocene. Possible reactions of the nickelocene anion $Ni(C_5H_5)_2^-$ with a variety of simple molecules were investigated with the purpose of observing ligand displacement reactions. When 10^{-6} Torr of nickelocene was mixed with a (10-20)-fold excess of CO, HCl, NO, HCN, and NH_3, no change in the negative-ion mass spectrum was observed. The failure to observe any ligand transfer or condensation reactions may be due to two factors: the reactions were too slow to observe ($k < 10^{-11}$ cm^3 $molecule^{-1}$

Table II. Equilibrium Constants and Proton Affinities Employed to Establish PA[$Ni(C_5H_5)_2$][a]

		PA	
Equilibrium	K	Amine[b]	$Ni(C_5H_5)_2$[c]
$HNi(C_5H_5)_2^+ + (CH_3)_3N \rightleftharpoons (CH_3)_3NH^+ + Ni(C_5H_5)_2$	14.2	220.6	218.5
$HNi(C_5H_5)_2^+ + (C_2H_5)_2NH \rightleftharpoons (C_2H_5)_2NH_2^+ + Ni(C_5H_5)_2$	11.9	221.2	219.2

[a] All values in kcal/mol. [b] See Table III. [c] Calculated from PA(amine) and the measured equilibrium constant and corrected for entropy effects.

s^{-1}), or the strength of the metal–cyclopentadienyl bond in $Ni(C_5H_5)_2^-$ is so great as to make the ion unreactive.

Gas-Phase Basicity of Nickelocene. Mixtures of nickelocene with molecules having a range of base strengths were examined to determine the preferred direction of proton-transfer reactions. Included were the molecules CH_3CHO, $(CH_3)_2O$, furan, $(C_2H_5)_2O$, $(i\text{-}C_3H_7)_2O$, $CH_3N{=}NCH_3$, CH_3NH_2, $C_2H_5NH_2$, $(CH_3)_2NH$, pyridine, $(CH_3)_3N$, $(C_2H_5)_2NH$, and $(C_2H_5)_3N$. Proton transfer occurs to produce protonated nickelocene, $HNi(C_5H_5)_2^+$, exclusively for all compounds except $(CH_3)_3N$, $(C_2H_5)_2NH$, and $(C_2H_5)_3N$. With $(CH_3)_3N$ and $(C_2H_5)NH$, equilibria 7 and 8 were identified

$$HNi(C_5H_5)_2^+ + (CH_3)_3N \rightleftharpoons (CH_3)_3NH^+ + Ni(C_5H_5)_2 \qquad (7)$$

$$HNi(C_5H_5)_2^+ + (C_2H_5)_2NH \rightleftharpoons (C_2H_5)_2NH_2^+ + Ni(C_5H_5)_2 \qquad (8)$$

and verified by double resonance,[2b,16] while with $(C_2H_5)_3N$ the reaction favored $(C_2H_5)_3NH^+$.

The proton affinity of a molecule M, PA(M), is defined as the negative of the enthalpy change for the gas-phase reaction $M + H^+ \rightarrow MH^+$ and represents a quantitative measure of the intrinsic basicity.[2b,27] From the equilibrium constants for the gas-phase proton-transfer reactions 7 and 8, free energies of protonation may be obtained. Kebarle has observed the temperature dependence of equilibrium proton-transfer reactions to be slight,[28,29] and the only significant entropy factor is expected to be due to changes in symmetry number.[30] From the known proton affinities of $(CH_3)_3N$ and $(C_2H_5)_2NH$[31] and the equilibrium constants for reactions 7 and 8, the proton affinity of nickelocene is established as 218.9 ± 1.0 kcal/mol, corresponding to $\Delta H_f[HNi(C_5H_5)_2^+] = 228.6 \pm 1.0$ kcal/mol.[22] Table II presents the equilibrium constants and proton affinities of $(CH_3)_3N$, $(C_2H_5)_2NH$, and nickelocene; Table III lists the proton affinities of the alkylamines,[31] $Ni(C_5H_5)_2$, $Fe(C_5H_5)_2$,[6] and $Fe(CO)_5$,[9] for comparison. The exceptionally high basicity of nickelocene is due, in part, to its low ionization potential[14] which allows for increased electron-donating ability to H^+.[2b]

In each of the mixtures used to determine gas-phase basicities, the possibility of ligand displacement or other condensation reactions was examined. Only with acetaldehyde were such reactions observed, with ferrocene and nickelocene exhibiting quite different reactivities, illustrated by eq 9 and 10. While the ferrocene molecular ion reacts with a threefold

$$Fe(C_5H_5)_2^+ + CD_3CDO \rightarrow (CD_3CO)Fe(C_5H_5)_2^+ + D \qquad (9)$$

$$Ni(C_5H_5)_2 + CD_3CDOD^+ \rightarrow (CD_3CDOD)Ni(C_5H_5)_2^+ \qquad (10)$$

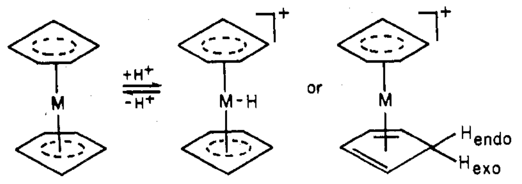
excess of acetaldehyde-d_4 to produce the $(CD_3CO)Fe(C_5H_5)_2^+$ ion (reaction 9), this process is not observed with nickelocene. Conversely, nickelocene readily forms a long-lived complex with protonated acetaldehyde, reaction 10, while ferrocene does not.

Site of Protonation. While ferrocene is known to protonate on the metal atom in solution, resulting in species I (M = Fe), ring protonation must also occur since ferrocene undergoes ring proton exchange in strongly acidic media.[32] Court and Werner produced the $Ni(C_5H_5)(C_5H_6)^+$ cation II (M = Ni) in a solution of HF and nickelocene.[25] The metal atoms in both of the preferred species, $HFe(C_5H_5)_2^+$ and $Ni(C_5H_5)(C_5H_6)^+$, possess an 18-electron inert-gas configuration.

Table III. Proton Affinities of Alkylamines, $Ni(C_5H_5)_2$, $Fe(C_5H_5)_2$, and $Fe(CO)_5$

Molecule	ΔPA-(M)[a]	Molecule	ΔPA-(M)[a]	Molecule	ΔPA-(M)[a]
$(C_2H_5)_3N$	26.3	$(CH_3)_2NH$	15.4	$Fe(C_5H_5)_2$	6[c]
$(C_2H_5)_2NH$	20.2	$C_2H_5NH_2$	11.8	NH_3	0.0[d]
$(CH_3)_3N$	19.6	CH_3NH_2	9.3	$Fe(CO)_5$	−3[e]
$Ni(C_5H_5)_2$	17.9[b]				

[a] All values in kcal/mol relative to NH_3. Except as noted, all data are from ref 31. [b] This work. [c] Reference 6. [d] PA(NH_3) is taken as 201 ± 1 kcal/mol. This is somewhat lower than the value of 207 kcal/mol which has been widely used in the literature. Recent experiments indicate a lower value for PA(NH_3) is more appropriate with 201 ± 1 kcal/mol closer to the true value: R. H. Staley, I. Koppel, J. F. Wulf, J. L. Beauchamp, and R. W. Taft, unpublished results; also P. Kebarle, unpublished results. [e] Reference 9.



I II

Experiments to determine the site of gas-phase protonation of nickelocene and ferrocene were inconclusive. When mixtures of the metallocene (M = Ni, Fe) with a tenfold excess of D_2O were examined using ICR trapped-ion techniques,[15] abundant $DM(C_5H_5)_2^+$ ions resulted from the sequence of reactions 11 and 12, but no further incorporation of deuterium

$$D_2O^+ + D_2O \rightarrow D_3O^+ + OD \qquad (11)$$

$$D_3O^+ + M(C_5H_5)_2 \rightarrow DM(C_5H_5)_2^+ + D_2O \qquad (12)$$

was observed.[33] In addition, the thermoneutral exchange reaction (13), which would be indicative of ring protonation,

$$M(C_5H_5)(C_5H_5D)^+ + M(C_5H_5)_2 \rightarrow M(C_5H_5)(C_5H_6)^+ + M(C_5H_5)(C_5H_4D) \qquad (13)$$

was not observed for either nickelocene or ferrocene. Thermoneutral exchange reactions such as illustrated in eq 14 are observed for alcohols,[34] amines,[34] and substituted

$$(CD_3)_2NHD^+ + (CD_3)_2NH \rightarrow (CD_3)_2NH_2^+ + (CD_3)_2ND \qquad (14)$$

benzenes[35] and provide information relating to the site of protonation. A possible complication occurs with the metallocenes, however, because the labile methylene hydrogens on the protonated cyclopentadienyl ring, H_{endo} and H_{exo}, are not equivalent.

A small amount of $(C_2H_5)_3N$ was added to the mixture of $Ni(C_5H_5)_2$ with D_2O to remove either a proton or a deuteron from $DNi(C_5H_5)_2^+$ by proton (deuteron) transfer, yielding $(C_2H_5)_3N(H,D)^+$ as indicated in reactions 15 and 16. The

$$DNi(C_5H_5)_2^+ + (C_2H_5)_3N \rightarrow (C_2H_5)_3ND^+ + (C_2H_5)_2Ni \qquad (15)$$

$$Ni(C_5H_5)(C_5H_5D)^+ + (C_2H_5)_3N \rightarrow (C_2H_5)_3NH^+ + Ni(C_5H_5)(C_5H_4D) \qquad (16)$$

results were obscured by the many competing protonation and deuteration reactions to produce $(C_2H_5)_3N(H,D)^+$ and by the slow rate of reactions 15 and 16, both of which render the double-resonance experiments inconclusive.

The homolytic bond dissociation energy, $D(M^+{-}H)$, is defined as the enthalpy change for the reaction $MH^+ \rightarrow M^+ + H$ and is related to the proton affinity of M by eq 17, where

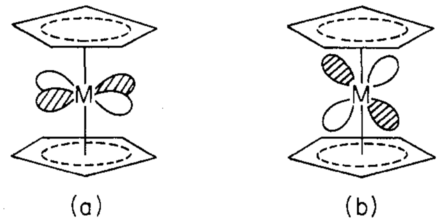


Figure 2. Illustrated symmetry of highest occupied molecular orbitals of metallocene radical cations: (a) $3d_{xy}$ component of e_{2g} orbital of $Fe(C_5H_5)_2^{+}$; (b) $3d_{xz}$ component of e_{1g} orbital of $Ni(C_5H_5)_2^{+}$.

$$PA(M) - D(M^{+}\text{-}H) = IP(H) - IP(M) \qquad (17)$$

the indicated ionization potentials refer to the adiabatic values. Homolytic bond energies are useful for correlating gas-phase basicities because they generally remain constant for a homologous series, yielding a linear relationship between PA(M) and IP(M).[2b,36,37] In studies to date of systems which exhibit this behavior, the highest occupied molecular orbital (HOMO), corresponding to the lowest ionization potential, is involved in bond formation between the radical cation M^+ and H.[2b,36–38] The He(I) photoelectron spectrum of nickelocene reveals the first adiabatic IP at 6.2 ± 0.1 eV, which corresponds to the removal of an electron from the doubly occupied e_{1g} orbital.[14a] Combining this value with PA[$Ni(C_5H_5)_2$] = 218.9 ± 1.0 kcal/mol measured in this study gives $D[Ni(C_5H_5)_2^{+}\text{–}H] = 48.3 \pm 3$ kcal/mol. This represents the energy released combining the nickelocene radical cation in its lowest electronic state with an H atom to give protonated nickelocene. The calculated bond energy is extraordinarily low compared with those for other organic and simple inorganic molecules (which generally range between 80 and 130 kcal/mol)[2b] and explains why the parent ion does not react to form the conjugate acid in nickelocene (Figure 1). By comparison, $D[Fe(C_5H_5)_2^{+}\text{–}H] = 56 \pm 6$ kcal/mol[6] and $D[Fe(CO)_5^{+}\text{–}H] = 74 \pm 3$ kcal/mol.[9] While the values of $D(M^{+}\text{–}H)$ for nickelocene and ferrocene are surprisingly close, the agreement must be considered accidental as these two metallocenes are certainly not members of a homologous series, particularly if nickelocene protonates on the ring, to give an ion of structure II, while ferrocene protonates on the metal to give I.

It is instructive to consider the HOMO of ferrocene and nickelocene radical cations.[39] Figure 2 shows that, in $Fe(C_5H_5)_2^{+}$, the HOMO is of e_{2g} symmetry which facilitates formation of the $M^{+}\text{–}H$ bond. The e_{1g} symmetry of the HOMO of $Ni(C_5H_5)_2^{+}$ does not allow for its participation in the formation of an $M^{+}\text{–}H$ bond if nickelocene were to protonate on the metal. For these reasons the calculated $D(M^{+}\text{–}H)$ homolytic bond dissocation energy loses its significance in comparison to that of ferrocene and serves only to describe the thermochemical changes associated with bond formation.

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